644

INTERLABORATORY STUDY 88-3

VALIDATION OF A METHOD FOR RESIN AND FATTY ACIDS

SPIKED SAMPLES PREPARED IN REAGENT WATER AND PULP AND PAPER MILL EFFLUENTS

NOVEMBER 1988

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Report Prepared by:
Laboratory Services Branch
Ontario Ministry of the Environment

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Table of Contents

1 OVERVIEW OF THE INTERLABORATORY STUDIES TO ASSESS THE METHOD FOR RESIN AND FATTY ACIDS 1

2 SUMMARY AND CONCLUSIONS 3

3 INTRODUCTION 4

4 PROCEDURE 4
- 4.1 Preparation of Samples 4
- 4.2 Sample Distribution 6
- 4.3 Analytical Methodology 6
- 4.4 Data Handling 6

5 RESULTS AND DISCUSSION 8

6 REFERENCES 10

7 APPENDIX 1 - FULL DATA SET 11

8 APPENDIX 2 - LIST OF PARTICIPANTS AND CORRESPONDENCE 12

1 OVERVIEW OF THE INTERLABORATORY STUDIES TO ASSESS THE METHOD FOR RESIN AND FATTY ACIDS

In 1987, an Analytical Working Group (AWG) was formed to develop an improved analytical procedure for the analysis of Resin and Fatty Acids (MISA Group 26 and PP3). The AWG consisted of representatives from the Ontario Forest Industries Association (OFIA), Ontario Ministry of the Environment (MOE), and Environment Canada (EC), under the MISA program.

Initial work was done during 1987 to assess the stability of standards, the pH adjustments to be made prior to extraction, column conditions, and other instrumental conditions. The results have been reported elsewhere (3). In May 1988, the Method for Resin and Fatty Acids, Draft 3 (4) was ready to be validated by means of an interlaboratory collaborative study. A series of four separate studies were undertaken to assess the new method.

Interlaboratory Study 88-2A

This was the first study initiated to validate the performance of the Method for Resin and Fatty Acids, Draft 3 (4). Ampoules were distributed in June 1988. Four ampouled standards were provided to each participant, two to be spiked into reagent water and processed through the entire method, and two for direct methylation and injection into the analytical instrument.

The results indicated that the Draft Method produces similar results from all of the participants. Differences between laboratories may be attributed to differences in calibration of Dehydroabietic Acid. Some parameters are not recovered as well as others. This may be due to the difficulty of assuring the purity of the standards.

The results from Interlaboratory Study 88-2A demonstrated that the Draft Method works, as long as the calibration of Dehydroabietic Acid is carried out in a precise and accurate manner. The initial review of the raw data raised concern among the AWG regarding the use of two different solvents to prepare the standard solutions. A small follow-up study was required (see Interlaboratory Study 88-2B below), using fresh stock solutions, to assess whether some of the differences in performance were introduced by the different solvents used to prepared the standards.

Interlaboratory Study 88-2B

This was the second study to validate the performance of the Method for Resin and Fatty Acids, and was the follow-up to Interlaboratory Study 88-2A. Ampoules were distributed in August 1988. Four laboratories received two ampouled standards for direct methylation and instrumental injection. Each ampouled standard consisted of three parameters, one standard prepared in methanol and one standard prepared in methyl-t-butyl ether (MTBE). A third ampouled standard, consisting of the same three parameters dissolved in MTBE, but pre-methylated prior to sealing in the ampoules, was also provided to each laboratory. The third standard was to be used to verify that the four laboratories agreed in their calibration.

The results demonstrated that there was no significant difference between the mean of the results from standard prepared in methanol versus the mean of the results from the standard prepared in MTBE.

There was also no significant difference between the mean of the results from the standard prepared in MTBE that was not pre-methylated, versus the mean of the results from the standard prepared in MTBE that was pre-methylated.

Interlaboratory Study 88-3 (This Report)

This was the third interlaboratory study to validate the performance of the Method for Resin and Fatty Acids, Draft 3 (4). A set of ten samples was distributed to the participants in November 1988. The sample sets consisted of a High Spike, Low Spike, and Blank of Reagent Water, a High Spike, Low Spike, and Blank of Pulp and Paper Mill Effluent #1, a High Spike, Low Spike, and Blank of Pulp and Paper Mill Effluent #2, and one unspiked Pulp and Paper Mill Effluent #3.

The results indicated that the laboratories were able to recover the spiked Resin and Fatty Acids from the reagent water samples. Results from the two different spiked pulp and paper mill effluents produced very variable results, with very few laboratories reporting results from the low spike effluent samples. Reasonable consistency of results between laboratories was achieved for the unspiked Pulp and Paper Mill Effluent #3.

The variability of the results suggested that there may have been problems recovering the spiked Resin and Fatty Acids from the effluent samples. It was decided to repeat this study in the spring of 1989. This study was reported as Interlaboratory Study 89-2 (see below).

Interlaboratory Study 89-2

This was the fourth (and final) interlaboratory study to validate the performance of the Method for Resin and Fatty Acids, Draft 3 (4). A set of nine samples was distributed to the participants in March 1989. The sample sets consisted of a High Spike, Low Spike, and Blank in Reagent Water, a High Spike, Low Spike, and Blank of Pulp and Paper Mill Effluent #1, a High Spike, Low Spike, and Blank of Pulp and Paper Mill Effluent #2.

The results indicated that the laboratories were able to recover the spiked Resin and Fatty Acids from the reagent water samples. Results from the two different spiked pulp and paper mill effluents produced very variable results, with very few laboratories reporting results from Pulp and Paper Mill Effluent #2. The same sources of pulp and paper mill effluent were used for both Interlaboratory Study 88-3 and this study (89-2). After reviewing the mill processes, it was noted that Pulp and Paper Mill Effluent #2 was a biologically treated effluent. The absence of recovery of the spiked Resin and Fatty Acids from this effluent in both studies, suggests that the effluent was still biologically active and degraded the spiking material.

Separate reports have been prepared for each study.

2 SUMMARY AND CONCLUSIONS

Interlaboratory Study 88-3 was the third study to validate the performance of the Method for Resin and Fatty Acids, Draft 3 (4). It was initiated by the Quality Assurance Office, Laboratory Services Branch of the Ontario Ministry of the Environment, at the request of the Analytical Working Group (AWG) of the Pulp and Paper Sector under the MISA program.

Participants were provided with a set of ten samples, consisting of a Blank, Low and High Spike in Reagent Water, a Blank, Low and High Spike in Pulp and Paper Mill Effluent #1, a Blank, Low and High Spike in Pulp and Paper Mill Effluent #2, and a Unspiked (Blank) Pulp and Paper Mill Effluent #3. The same nine laboratories who were invited to participate in Interlaboratory Study 88-2A (5) were invited to participate in this study. Results were reported from six participants

The results from this study demonstrate that the Draft Method is suitable for the analysis of samples of reagent water spiked with Resin and Fatty Acids. The results from the untreated effluent sample (Sample 4A) also demonstrate that the Draft Method produces consistent results between laboratories in a "real" sample, when Resin and Fatty Acids are present.

The results from the spiked treated effluent samples were very variable. Low recoveries of the spiking material were observed from the four spiked effluent samples. Review of the treatment processes at the two pulp and paper mills suggest that the effluents may still have been biologically active and therefore degraded the spiking material.

The preliminary review of the raw data set by the AWG raised concern that the Draft Method was not effective for the analysis of spiked effluent samples. The AWG requested that the study be repeated, using fresh stock spiking solutions. It was felt that it was not necessary to repeat the analysis of the untreated effluent sample. The repeat study was carried out in March 1989 and reported as Interlaboratory Study 89-2.

3 INTRODUCTION

In June 1988, Interlaboratory Study 88-2A was conducted to validate the interlaboratory performance of the Method for Resin and Fatty Acids, Draft 3 (4), by the Quality Assurance Office, Laboratory Services Branch of the Ontario Ministry of the Environment. The results from this study have been reported elsewhere (5). A follow-up study was required to assess whether the different solvents used in the ampoule preparation affected the variability of the results. This second study was conducted in August 1988 and reported as Interlaboratory Study 88-2B (6). The results indicated that the solvent used to prepare the ampoules did not affect the variability of the results.

The Analytical Working Group (AWG) of the MISA Pulp and Paper Sector agreed to proceed with the next stage of the method validation. Interlaboratory Study 88-3 was designed to assess interlaboratory variability in the analysis of spiked reagent water and spiked pulp and paper mill effluents. Two treated pulp and paper mill effluents were provided for spiking with known amounts of Resin and Fatty Acids. A third untreated pulp and paper mill effluent was provided as an extra sample for between laboratory comparison. It was was not spiked with the Resin and Fatty Acid standard solution used for the reagent water and two treated effluent samples.

Nine laboratories were invited to participate in this study: three government laboratories (provincial and federal), two industrial laboratories, and four commercial laboratories. All participants were required to agree to use the Draft Method for the analysis of the samples. If possible, the participants were asked to perform the analysis in duplicate. Not all of the participants were able to report final results for all of the samples (see Section 4.4). A list of invited participants is included in Appendix 2.

Details of sample preparation and distribution are given in Sections 4.1 and 4.2. Analytical methodology and data handling are presented in Sections 4.3 and 4.4. Final results are presented and discussed in Section 5.0. Each participant was assigned a unique identification code to maintain confidentiality.

4 PROCEDURE

4.1 Preparation of Samples

Deionized, distilled water was used as the matrix for the reagent water spikes. Care was taken that no plastic materials came into contact with the water when transferring to one litre amber sample bottles. To each bottle, 800 mL of water was added by weight (800 g ±2 g). Unspiked bottles were labelled "1A". The appropriate amount of Resin and Fatty Acid Stock Solution was dispensed into the bottles for the low and high spikes. The low spike was labelled "1B" and the high spike was labelled "1C".

Twenty litres of treated effluent was received from each of two different pulp and paper mills. The effluents were received in 2.5 litre bo·tles. All the effluent from one mill was poured into a clean, 50 litre, stainless steel tank, whicn had a spout. A stainless steel stirrer was used for one hour to homogenized the effluent. To each one litre amber sample bottle, 800 mL of effluent was transferred by weight (800 g ±2 g). The procedure was repeated for the second effluent. The appropriate amount of Resin and Fatty Acid Stock Solution was dispensed into the bottles for the low and high spikes. For Effluent #1 the samples were labelled as follows: unspiked - "2A", low spike - "2B", and high spike - "2C". For Effluent #2 the samples were labelled as follows: unspiked - "3A", low spike - "3B", and high spike - "3C".

Two different spiking solutions were used for the low and high spikes, because of the different concentration levels. Table 1 lists the parameters used for all of the low spikes (reagent water and Effluents #1 and #2). Table 2 lists the parameters used for all of the high spikes (reagent water and Effluents #1 and #2). The solution used for the low spikes was prepared in methanol. The solution used for the high spikes was prepared in methyl-t-butyl ether (MTBE).

TABLE 1 - Parameter List for Low Spikes

Linolenic Acid
Oleic Acid
Sandaracopimaric Acid
Isopimaric Acid
Palustric Acid
Levopimaric Acid
Dehydroabietic Acid
Abietic Acid
Neoabietic Acid
9,10-Dichlorostearic Acid
Chlorodehydroabietic Acid
Dichlorodehydroabietic Acid

TABLE 2 - Parameter List for High Spikes

Oleic Acid
Sandaracopimaric Acid
Isopimaric Acid
Palustric Acid
Levopimaric Acid
Dehydroabietic Acid
Abietic Acid
Neoabietic Acid
9,10-Dichlorostearic Acid
Chlorodehydroabietic Acid
Dichlorodehydroabietic Acid

Ten litres of untreated effluent was received from a third pulp and paper mill. This effluent was homogenized using the same procedure as used for Effluents #1 and #2. A set of unspiked 800 mL samples was prepared using Effluent #3 and labelled as sample "4A".

4.2 Sample Distribution

The invited participants received a letter of notification in November, 1988. A copy is included in Appendix 2. All laboratories verified their participation by telephone. A list of invited participants is included in Appendix 2.

A set of ten samples, one each of 1A, 1B, 1C, 2A, 2B, 2C, 3A, 3B, 3C, and 4A, were packaged in boxes and shipped via Purolator courier on November 29, 1988. Each package included a cover letter and instruction sheet. Copies are included in Appendix 2.

Laboratory 6008 notified the QA Office that one box of samples was received broken. A second set of effluent samples (2A, 2B, 2C, 3A, 3B, 3C, and 4A) was prepared on December 2, 1988 and shipped to Laboratory 6008. Some of the first set of effluent samples were still intact. Laboratory 6008 stated that they would analyze all of the samples that they received. Results from the first set are reported as 6008A. Results from the second set are reported as 6008B.

4.3 Analytical Methodology

All participating laboratories were required to use the Draft Method for Resin and Fatty Acids (4). The analytical principles of this method are described in Schedule 2 of the Draft Pulp and Paper Regulation (2). All participants were asked to provide details of any modifications they may have made to the method. Each participant was asked to analyze each sample in duplicate, if possible.

4.4 Data Handling

Results were submitted to the QA Office of Laboratory Services Branch, MOE in written form by mail. All data were manually entered into an electronic spreadsheet. Blank spaces were left when a laboratory did not report results for a parameter that was present in the spiking material (i.e. the participant did not have the appropriate calibration standard). A value of "0" was used for the purpose of numerical evaluation for values reported as "Not Detected" by the laboratories.

One industrial laboratory was unable to participate in the last minute, and requested not to receive a sample set. Two commercial laboratories did not report any results. One commercial lab-

oratory stated that they had a computer malfunction and lost their data. The other commercial laboratory did not provide any explanations as to why they were unable to submit results. Final percent participation was 75% (excluding the one industrial laboratory).

Between-laboratory variability was determined by calculating the mean and standard deviation of the results reported. All results are presented in Appendix 1, Table 1.

Results were converted to percent recovery based on the design value of the spiking material. These values are presented in Appendix 1, Table 2.

Included in Appendix 1 are bar graphs of the recovery for each parameter from each participating laboratory (Figures 1-6). Each graph represents a different sample and the parameters are arranged left to right in order of gas chromatographic elution, using a DB-1 fused silica capillary column, as specified in the Draft Method (4). Outliers were not deleted from the data set when preparing the graphs. All results are presented as percent recovery relative to the design value. When a laboratory submitted duplicate results for a sample, the mean of the duplicates was used for these graphs.

In Interlaboratory Study 88-2A (5) it was observed that interlaboratory bias is introduced due to the differences in calibration of Dehydroabietic Acid (DHA). DHA is used as the reference point when calibrating the instrument, and all other analytical results are calculated using the relative response factor of this parameter (4). The percent recovery data from Samples 1B and 1C (Low and High Spikes in Reagent Water) were normalized relative to the results for DHA reported by each participant, to remove the effect of laboratory differences in calibration. The normalized results are presented in bar graphs for each parameter in Appendix 1 (Figures 7-16). This was not done for the spiked effluent samples (2B, 2C, 3B, and 3C) as there was insufficient data to do so.

Sample 4A was an unspiked effluent sample, with unknown amounts of Resin and Fatty Acids present. The results tabulated in Table 1, Appendix 1 are presented as a bar graph in Figure 17. The duplicate results are reported separately for each participant.

5 RESULTS AND DISCUSSION

The raw results (Table 1, Appendix 1) were converted to percent recovery of the design values (Table 2, Appendix 1) to assess the performance of each participant. Preliminary evaluation of the results for the spiked Reagent Water samples (1B and 1C), suggest parameter or laboratory biases, similar to those observed for the percent recovery results in Interlaboratory Study 88-2A (5). To remove laboratory bias, the results from Samples 1B and 1C (High and Low Spikes, Reagent Water) were normalized relative to the value for DHA reported by each participant.

The normalized results (Figures 7-16, Appendix 1) demonstrate consistent performance between laboratories for many of the parameters. Some parameters such as Neoabietic Acid (Figure 13) and Dichlorodehydroabietic Acid (Figure 14) display variable performance. This may be due to the difficulty of obtaining pure, stable materials to prepare the spiking solutions, as has been observed previously (3, 5).

The normalized results (Figures 7-16) suggest a difference in the recovery of the high spike (Sample 1C) versus the low spike (Sample 1B). Based on the design values, better recovery was obtained from the low spike samples. The spiking standard for the low spikes was prepared in methanol, while the spiking standard for the high spikes was prepared in MTBE (see Section 4.1). Methanol is more soluble in water than MTBE. Therefore the aliquot of standard in methanol would be better mixed in Sample 1B than the aliquot of standard in MTBE for Sample 1C. The Draft Method requires only a 50 mL portion of sample for analysis (4). If the standard prepared with MTBE was not well dispersed in the high spike samples (1C), the 50 mL portion taken for analysis may not have contained the expected amount of spike material. Laboratory 6004 commented on the possible problems associated with using MTBE for the spiking material when they reported their results.

The results from the spiked effluent samples (2B, 2C, 3B, and 3C) displayed considerable variability. All of the participants commented on the low levels of Resin and Fatty Acids in these four samples. Several participants noted that Samples 2A, 2B, and 2C had particulate matter (Effluent #1). The low recoveries in Samples 2B and 2C from all of the participants may be due to the spiking material adhering to the particulate matter.

Both of the treated effluents provided for the study were from pulp and paper mills that have biological treatment processes. This is the treatment process recommended for removal of Resin and Fatty Acids prior to discharging the effluent (2). The low recovery of the spiked material from Samples 2B, 2C, 3B, and 3C may be due to the effluents still being active and degrading the spiking material.

The results from Sample 4A (Unspiked Effluent #3) demonstrate consistent performance between laboratories, except for Laboratory 6007. Laboratory 6007 reported their results late, and included a note with their results indicating that they had exceeded the time limit specified in the MISA regulation (2) for the initiation of analysis. This would explain their low results relative to the other participants. Figure 17 presents the results in graphical form. The results also demonstrate good within-laboratory precision (Laboratory 6005 was the only participant not to report duplicate results).

The results from this study demonstrate that the Draft Method is suitable for the analysis of samples of reagent water spiked with Resin and Fatty Acids. The results from the untreated effluent sample (Sample 4A) also demonstrate that the Draft Method produces consistent results between laboratories in a "real" sample, when Resin and Fatty Acids are present.

The preliminary review of the raw data set by the AWG raised concern that the Draft Method was not effective for the analysis of spiked effluent samples. The AWG requested that the study be repeated, using fresh stock spiking solutions. It was felt that it was not necessary to repeat the analysis of the untreated effluent sample. The repeat study was carried out in March 1989 and reported as Interlaboratory Study 89-2.

6 REFERENCES

1. Ontario Regulation 695/88 as amended to Ontario Regulation 533/89 under the Environmental Protection Act; Effluent Monitoring - General.

2. The Development Document for the Draft Effluent Monitoring Regulation for the Pulp and Paper Sector, March 1989; ISBN 0-7729-4764-3.

3. Minutes from the OFIA/MOE/EC Analytical Working Group, 1987 and 1988, inclusive. (Copies of all minutes were reported to the Joint Technical Committee for the Pulp and Paper Sector.)

4. Method for Resin and Fatty Acids; OFIA/MOE/EC Analytical Working Group; Draft, May 5, 1988.

5. Interlaboratory Study 88-2A; Validation of a Method for Resin and Fatty Acids; Ampoules for Spiking Reagent Water and Direct Methylation; February 1990, ISBN 0-7729-6749-0.

6. Interlaboratory Study 88-2B; Validation of a Method for Resin and Fatty Acids; Ampouled Standards in Two Different Solvents for Direct Methylation and Instrumental Injection; February 1990, ISBN 0-7729-6750-4.

7 APPENDIX 1 - FULL DATA SET

Table 1	Results for Interlaboratory Study 88-3
Table 2	Results for interlaboratory Study 88-3, Expressed as Percent Recovery of the Design Value
Figure 1	Sample 1B - Low Spike, Reagent Water
Figure 2	Sample 1C - High Spike, Reagent Water
Figure 3	Sample 2B - Low Spike, Effluent #1
Figure 4	Sample 2C - High Spike, Effluent #1
Figure 5	Sample 3B - Low Spike, Effluent #2
Figure 6	Sample 3C - High Spike, Effluent #2
Figure 7	Linolenic Acid Normalized to DHA (Samples 1B and 1C)
Figure 8	Oleic Acid Normalized to DHA (Samples 1B and 1C)
Figure 9	Sandaracopimaric Acid Normalized to DHA (Samples 1B and 1C)
Figure 10	Isopimaric Acid Normalized to DHA (Samples 1B and 1C)
Figure 11	Palustric & Levopimaric Acids Normalized to DHA (Samples 1B and 1C)
Figure 12	Abietic Acid Normalized to DHA (Samples 1B and 1C)
Figure 13	Neoabietic Acid Normalized to DHA (Samples 1B and 1C)
Figure 14	Chlorodehydroabietic Acid Normalized to DHA (Samples 1B and 1C)
Figure 15	9,10-Dichlorostearic Acid Normalized to DHA (Samples 1B and 1C)
Figure 16	Dichlorodehydroabietic Acid Normalized to DHA (Samples 1B and 1C)

TABLE 1 - INTERLABORATORY STUDY 88-3: RESIN AND FATTY ACIDS
RESULTS EXPRESSED AS ppb

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SAMPLE#	PARAMETER	DESIGN (ppb)	LABORATORY NUMBER 6001 RES1	6001 RES2	6004 RES1	6004 RES2	6005	6007 RES1	6007 RES2	6008A RES1	6008A RES2	6008B RES1	6008B RES2	6009 RES1	6009 RES2	MEAN	RANGE MIN	RANGE MAX	STD DEV
1A	LINOLENIC	-								-	-								
1A	OLEIC	-								-	-			12	20				
1A	SANDARACOPIMARIC	-								-	-								
1A	ISOPIMARIC	-								-	-								
1A	PALUSTRIC/LEVOPIMARIC	-								-	-								
1A	DYHYDROABIETIC	-								-	-								
1A	ABIETIC	-								-	-								
1A	NEOABIETIC	-							7.2	-	-								
1A	CHLORODEHYDROABIETIC	-								-	-								
1A	9,10-DICHLOROSTEARIC	-								-	-								
1A	DICHLORODEHYDROABIETIC	-								-	-								
1A	α-METHYLPODOCARPIC(ZREC)		68.2%	94.0%	98.0%	97.0%		76.4%	77.6%			90.7%	87.1%	101.0%	78.0%				
1B	LINOLENIC	51.0	44.8	45.9	0	0	18	41.6	-	-	-	23.1	20.3	48	54	29.6	0.0	54.0	20.0
1B	OLEIC	52.0	47.9	49.6	31	37	21	27.8	-	-	-	26.4	29.5	33	41	34.4	21.0	49.6	9.4
1B	SANDARACOPIMARIC	54.0	46.1	46.6	35	38	28	42.5	-	-	-	36.2	29.3	42	46	39.0	28.0	46.6	6.8
1B	ISOPIMARIC	52.0	59.6	59	38	44	35	59.4	-	-	-	42.4	37.2	47	52	47.4	35.0	59.6	9.6
1B	PALUSTRIC/LEVOPIMARIC	103.1	46.4	43.9	9	0	50	28.2	-	-	-	21.4	19.7	29	26	28.2	8.0	50.0	14.7
1B	DYHYDROABIETIC	53.5	91.1	64.8	0	0	56	92.9	-	-	-	56.5	50.9	65	79	55.6	0.0	92.9	32.6
1B	ABIETIC	50.8	19.2	19.3	86	103	12	15.2	-	-	-	14.8	13.1	14	12	30.9	12.0	103.0	33.9
1B	NEOABIETIC	51.3	11.5	0	7	12	27	0	-	-	-	16.5	21.8	19	0	11.5	0.0	27.0	9.7
1B	CHLORODEHYDROABIETIC	51.5	31.4	26.5	27	28	14	24.6	-	-	-	0	0	0	0	15.2	0.0	31.4	13.8
1B	9,10-DICHLOROSTEARIC	50.5	22.6	22.8	6	16	9	14.5	-	-	-			0	0	11.4	0.0	22.8	9.1
1B	DICHLORODEHYDROABIETIC	50.8	28.3	30	6	7	6	6.74	-	-	-	16.5	12.8	0	0	11.3	0.0	30.0	10.6
1B	α-METHYLPODOCARPIC(ZREC)		51.9%	87.1%	91.0%	93.0%		75.2%				91.2%	69.7%	97.0%	69.0%				
1C	OLEIC	502.0	207	196.3	14	26	5	22.7	-	-	-	17.8	24.6	58	85	65.6	5.0	207.0	75.4
1C	SANDARACOPIMARIC	503.5	333.6	331.3	56	58	34	71.9	-	-	-	51.8	52.5	76	93	115.8	34.0	333.6	115.3
1C	ISOPIMARIC	502.0	372	370.6	42	52	38	83.5	-	-	-	45.8	50.8	83	105	124.3	38.0	372.0	132.0
1C	PALUSTRIC/LEVOPIMARIC	1004.5	36.5	36.9	0	0	14	16.5	-	-	-	0	0	60	51	21.5	0.0	60.0	23.0
1C	DYHYDROABIETIC	502.0	840.1	841.6	0	0	233	318	-	-	-	244	256	200	231	316.4	0.0	841.6	295.7
1C	ABIETIC	503.0	37	35.1	312	332	10	20.2	-	-	-	0	10	41	36	83.3	0.0	332.0	126.6
1C	NEOABIETIC	502.0	0	0	17	23	5	0	-	-	-	0	0	0	0	4.5	0.0	23.0	8.4
1C	CHLORODEHYDROABIETIC	502.5	219.9	222.6	71	79	11	42.2	-	-	-	32.4	39.1	24	37	77.8	11.0	222.6	70.2
1C	9,10-DICHLOROSTEARIC	504.0	205.6	217.8	14	16	15	19.7	-	-	-			0	24	64.0	0.0	217.8	91.5
1C	DICHLORODEHYDROABIETIC	502.5	271.8	279.2	0	0	0	14.1	-	-	-	12.7	20.3	0	0	61.4	0.0	279.2	113.0
1C	α-METHYLPODOCARPIC(ZREC)		74.2%	94.5%	92.0%	96.0%		74.9%				72.1%	76.2%	114.0%	87.0%				

REAGENT WATER: 1A - UNSPIKED; 1B - LOW SPIKED; 1C - HIGH SPIKE
α METHYLPODOCARPIC ACID - SURROGATE STANDARD

DUPLICATE RESULTS: RES1 - REPLICATE #1, RES2 - REPLICATE #2

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SAMPLE#	PARAMETER	DESIGN (ppb)	LABORATORY NUMBER 6001 RES1	6001 RES2	6004 RES1	6004 RES2	6005	6007 RES1	6007 RES2	6008A RES1	6008A RES2	6008B RES1	6008B RES2	6009 RES1	6009 RES2	MEAN	RANGE MIN	RANGE MAX	STD DEV
2A	LINOLENIC	-							-	-	-								
2A	OLEIC	-						5.32	-	-	-			12					
2A	SANDARACOPIMARIC	-							-	-	-								
2A	ISOPIMARIC	-							-	-	-								
2A	PALUSTRIC/LEVOPIMARIC	-							-	-	-								
2A	DYHYDROABIETIC	-							-	-	-								
2A	ABIETIC	-							-	-	-								
2A	NEOABIETIC	-							-	-	-								
2A	CHLORODEHYDROABIETIC	-							-	-	-								
2A	9,10-DICHLOROSTEARIC	-							-	-	-								
2A	DICHLORODEHYDROABIETIC	-							-	-	-								
2A	o-METHYLPODOCARPIC(ZREC)		89.6%	95.1%	78.0%	112.0%		81.0%				80.1%	89.5%	110.0%	108.0%				
2B	LINOLENIC	51.0	0	0	0	0	0	0	-	-	-	0	0	0	0	0.0	0.0	0.0	0.0
2B	OLEIC	52.0	5.4	0	0	0	0	0	-	-	-	0	0	9	9	2.3	0.0	9.0	3.9
2B	SANDARACOPIMARIC	54.0	0	0	0	0	0	0	-	-	-	0	0	25	23	4.8	0.0	25.0	10.1
2B	ISOPIMARIC	52.0	0	0	0	0	0	0	-	-	-	0	0	32	31	6.3	0.0	32.0	13.3
2B	PALUSTRIC/LEVOPIMARIC	103.1	0	0	0	0	0	0	-	-	-	0	0	0	0	0.0	0.0	0.0	0.0
2B	DYHYDROABIETIC	53.5	0	0	0	0	0	0	-	-	-	6	0	23	0	2.3	0.0	23.0	7.3
2B	ABIETIC	50.8	0	0	0	0	0	0	-	-	-	0	0	0	0	0.0	0.0	0.0	0.0
2B	NEOABIETIC	51.3	0	0	0	0	0	0	-	-	-	0	0	0	0	0.0	0.0	0.0	0.0
2B	CHLORODEHYDROABIETIC	51.5	0	0	0	0	6	0	-	-	-	0	0	0	0	0.6	0.0	6.0	1.9
2B	9,10-DICHLOROSTEARIC	50.5	0	0	0	0	0	0	-	-	-			0	0	0.0	0.0	0.0	0.0
2B	DICHLORODEHYDROABIETIC	50.8	14.6	12.7	0	0	17	0	-	-	-	0	0	0	0	4.4	0.0	17.0	7.2
2B	o-METHYLPODOCARPIC(ZREC)		94.3%	96.3%	62.0%	110.0%		82.8%				87.5%	78.7%	99.0%	97.0%				
2C	OLEIC	502.0	18.1	27.3	38	21	8	10.4	-	23.5	-	28.3	25	192	98	44.5	8.0	192.0	54.6
2C	SANDARACOPIMARIC	503.5	24.4	68.5	44	30	18	9.48	-	42.2	-	43.2	38.3	244	126	62.6	9.5	244.0	67.8
2C	ISOPIMARIC	502.0	32.2	91	58	39	32	16.3	-	53	-	60.8	64.1	315	160	83.8	16.3	315.0	85.9
2C	PALUSTRIC/LEVOPIMARIC	1004.5	14.4	42.8	15	14	15	0	-	0	-	0	0	94	64	23.6	0.0	94.0	30.8
2C	DYHYDROABIETIC	502.0	49.3	119.8	58	38	37	20.6	-	73.6	-	72	74.3	447	237	111.5	20.6	447.0	126.0
2C	ABIETIC	503.0	10.4	30.4	116	78	10	4.44	-	0	-	0	0	107	54	36.0	0.0	116.0	43.7
2C	NEOABIETIC	502.0	0	7.7	41	20	0	0	-	0	-	0	0	23	20	10.2	0.0	41.0	13.9
2C	CHLORODEHYDROABIETIC	502.5	19.3	46.7	27	33	15	7.24	-	0	-	0	0	158	82	35.3	0.0	158.0	47.6
2C	9,10-DICHLOROSTEARIC	504.0	22.8	48.9	<5	<5	19	19.5	-		-			152	84	43.3	0.0	152.0	51.9
2C	DICHLORODEHYDROABIETIC	502.5	95.3	134.8	67	50	72	58.7	-	56.2	-	101	147	225	128	103.2	50.0	225.0	52.7
2C	o-METHYLPODOCARPIC(ZREC)		83.6%	87.4%	112.0%	103.0%		78.7%		84.5%		91.3%	89.8%	101.0%	76.0%				

PULP AND PAPER MILL EFFLUENT #1: 2B - UNSPIKED; 2A - LOW SPIKE; 2C - HIGH SPIKE DUPLICATE RESULTS: RES1 - REPLICATE #1, RES2 - REPLICATE #2
o-METHYLPODOCARPIC ACID - SURROGATE STANDARD

TABLE 1 - INTERLABORATORY STUDY 88-3: RESIN AND FATTY ACIDS
RESULTS EXPRESSED AS ppb

DISTRIBUTED: NOVEMBER 28, 1989

SAMPLE#	PARAMETER	DESIGN (ppb)	LABORATORY NUMBER 6001 RES1	6001 RES2	6004 RES1	6004 RES2	6005	6007 RES1	6007 RES2	6008A RES1	6008A RES2	6008B RES1	6008B RES2	6009 RES1	6009 RES2	MEAN	RANGE MIN	RANGE MAX	STD DEV
3A	LINOLENIC	-							-										
3A	OLEIC	-							-					10	14				
3A	SANDARACOPIMARIC	-							-										
3A	ISOPIMARIC	-	10.4						-										
3A	PALUSTRIC/LEVOPIMARIC	-							-										
3A	DYHYDROABIETIC	-							-										
3A	ABIETIC	-	7.3						-										
3A	NEOABIETIC	-						7.18	-										
3A	CHLORODEHYDROABIETIC	-							-										
3A	9,10-DICHLOROSTEARIC	-							-										
3A	DICHLORODEHYDROABIETIC	-							-										
3A	o-METHYLPODOCARPIC(%REC)		93.1%	94.0%	81.0%	75.0%		77.6%		82.5%	80.3%	76.7%	82.6%	105.0%	98.0%				
3B	LINOLENIC	51.0	0	0	232	236	0	0	-	0	0	0	0	0	-	42.5	0.0	236.0	98.7
3B	OLEIC	52.0	11.4	10.9	11	10	3	0	-	0	0	0	0	10	-	5.1	0.0	11.4	5.4
3B	SANDARACOPIMARIC	54.0	0	0	0	0	0	0	-	0	0	0	0	0	-	0.0	0.0	0.0	0.0
3B	ISOPIMARIC	52.0	13.5	0	0	30	0	8.17	-	0	0	0	0	0	-	4.7	0.0	30.0	9.9
3B	PALUSTRIC/LEVOPIMARIC	103.1	0	0	0	0	0	6.24	-	0	0	0	0	0	-	0.6	0.0	6.2	2.0
3B	DYHYDROABIETIC	53.5	0	0	17	0	0	7.34	-	0	0	0	0	0	-	2.2	0.0	17.0	5.6
3B	ABIETIC	50.8	6.2	0	0	0	0	0	-	0	0	0	0	0	-	0.6	0.0	6.2	2.0
3B	NEOABIETIC	51.3	0	0	0	0	0	0	-	0	0	0	0	0	-	0.0	0.0	0.0	0.0
3B	CHLORODEHYDROABIETIC	51.5	0	0	0	0	0	0	-	0	0	0	0	0	-	0.0	0.0	0.0	0.0
3B	9,10-DICHLOROSTEARIC	50.5	0	0	0	0	0	0	-					0	-	0.0	0.0	0.0	0.0
3B	DICHLORODEHYDROABIETIC	50.8	12.3	11	0	0	0	9.8	-	0	0	0	0	0	-	3.0	0.0	12.3	5.4
3B	o-METHYLPODOCARPIC(%REC)		93.6%	94.0%	68.0%	82.0%		82.6%		72.7%	88.2%	87.1%	85.7%	102.0%					
3C	LINOLENIC	-	0	0	49	208	0	0	-	0	0	0	0	0	0	21.4	0.0	208.0	63.0
3C	OLEIC	439.3	53.1	57.8	72	162	32	67.3	-	41.7	30.7	55.3	66.3	77	64	64.9	32.0	162.0	33.8
3C	SANDARACOPIMARIC	440.6	62.2	64.1	106	244	52	91.0	-	50.1	27	76.1	80.8	77	59	83.2	52.0	244.0	54.1
3C	ISOPIMARIC	439.3	91.8	93	155	354	91	147	-	70.1	44.7	97.6	102	106	81	119.4	70.1	354.0	79.8
3C	PALUSTRIC/LEVOPIMARIC	878.9	64.7	57.8	62	164	64	50.5	-	29.8	0	43.9	54.5	53	37	56.8	29.8	164.0	35.6
3C	DYHYDROABIETIC	439.3	136.3	118.7	117	256	99	193	-	96.5	64	129	144	134	106	142.8	96.5	256.0	47.1
3C	ABIETIC	440.1	39.8	34.9	266	600	33	49.9	-	0	0	38.1	37.7	51	35	98.8	0.0	600.0	177.8
3C	NEOABIETIC	439.3	18	14.3	128	45	22	0	-	0	0	0	0	27	20	22.9	0.0	128.0	37.0
3C	CHLORODEHYDROABIETIC	439.7	49.5	53.1	116	259	45	85.5	-	0	0	68.7	97.5	75	57	75.5	0.0	259.0	66.0
3C	9,10-DICHLOROSTEARIC	441.0	54.3	58.3	42	104	54	110	-					40	35	64.2	35.0	110.0	30.1
3C	DICHLORODEHYDROABIETIC	439.7	89.1	93.9	204	446	111	137	-	99.3	84	152	170	102	75	140.9	75.0	446.0	104.8
3C	o-METHYLPODOCARPIC(%REC)		86.0%	93.9%	73.0%	111.0%		73.3%		75.9%	87.6%	90.8%	88.7%	109.0%	84.0%				

PULP AND PAPER MILL EFFLUENT #2: 3A - UNSPIKED; 3B - LOW SPIKE; 3C - HIGH SPIKE DUPLICATE RESULTS: RES1 - REPLICATE #1, RES2 - REPLICATE #2
o-METHYLPODOCARPIC ACID - SURROGATE STANDARD

TABLE 1 - INTERLABORATORY STUDY 88-3: RESIN AND FATTY ACIDS
RESULTS EXPRESSED AS ppb

DISTRIBUTED: NOVEMBER 28, 1989

SAMPLE#	PARAMETER	DESIGN (ppb)	LABORATORY NUMBER 6001 RES1	6001 RES2	6004 RES1	6004 RES2	6005	6007 RES1	6007 RES2	6008A RES1	6008A RES2	6008B RES1	6008B RES2	6009 RES1	6009 RES2	MEAN	RANGE MIN	RANGE MAX	STD DEV
4A	LINOLENIC		0	0	92	110	0	0	0					15	15	25.0	0.0	110.0	43.3
4A	OLEIC		353.7	296	234	250	232	245	259	215	246	250	273	335	220	262.2	215.0	353.7	42.3
4A	SANDARACOPIMARIC		177.5	167.1	149	162	126	151	146	117	138	134	150	176	156	150.0	117.0	177.5	18.2
4A	ISOPIMARIC		346	319.1	320	354	237	297	311	242	286	275	310	351	301	303.8	237.0	354.0	37.2
4A	PALUSTRIC/LEVOPIMARIC		538.3	405	332	440	440	334	356	270	334	275	323	521	440	385.3	270.0	538.3	86.4
4A	DYHYDROABIETIC		1096.4	1049	1300	1440	880	0	0	790	938	937	1015	1084	1069	892.2	0.0	1440.0	430.4
4A	ABIETIC		1161	866.1	880	860	884	0	0	818	1021	979	1119	1069	944	815.5	0.0	1161.0	376.9
4A	NEOABIETIC		185.3	55.4	0	0	173	0	0	92.9	167	134	158	174	166	100.4	0.0	185.3	78.3
4A	CHLORODEHYDROABIETIC		0	0	0	0	0	10.2	0	0	0	0	0	0	0	0.8	0.0	10.2	2.8
4A	9,10-DICHLOROSTEARIC		0	0	0	0	5	64.5	42.3					0	0	12.4	0.0	64.5	23.9
4A	DICHLORODEHYDROABIETIC		0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0	0.0	0.0
4A	PALMITIC						68												
4A	PINOLENIC						236												
4A	PIMARIC		69.6	63.9	63	68	45									61.9	45.0	69.6	9.8
4A	LINOLEIC		431	376			327	312	347	0	0	0	0			199.2	0.0	431.0	191.9
4A	o-METHYLPODOCARPIC(%REC)		86.0%	96.8%	62.0%	56.0%		64.0%	64.6%	72.0%	90.1%	86.6%	93.1%	97.0%	106.0%				

PULP AND PAPER MILL EFFLUENT #3: 4A - UNSPIKED
o-METHYLPODOCARPIC ACID - SURROGATE STANDARD

DUPLICATE RESULTS: RES1 - REPLICATE #1, RES2 - REPLICATE #2

TABLE 2 - INTERLABORATORY STUDY 88-3: RESIN AND FATTY ACIDS
RESULTS EXPRESSED AS PERCENT RECOVERY OF DESIGN VALUE

DISTRIBUTED: NOVEMBER 28, 1988

SAMPLE#	PARAMETER	DESIGN (ppb)	LABORATORY NUMBER 6001 RES1	6001 RES2	6004 RES1	6004 RES2	6005 RES1	6007 RES1	6008A RES1	6008A RES2	6008B RES1	6008B RES2	6009 RES1	6009 RES2	MEAN	RANGE MIN	RANGE MAX
1B	LINOLENIC	51.0	88%	90%	0%	0%	35%	82%			45%	40%	94%	106%	58%	0%	106%
1B	OLEIC	52.0	92%	95%	60%	71%	40%	53%			51%	57%	63%	79%	66%	40%	95%
1B	SANDARACOPIMARIC	54.0	85%	86%	65%	70%	52%	79%			67%	54%	78%	85%	72%	52%	86%
1B	ISOPIMARIC	52.0	115%	113%	73%	85%	67%	114%			82%	72%	90%	100%	91%	67%	115%
1B	PALUSTRIC/LEVOPIMARIC	103.1	45%	43%	9%	0%	40%	27%			21%	19%	28%	25%	27%	8%	40%
1B	DYHYDROABIETIC	53.5	170%	121%	0%	0%	105%	174%			106%	95%	121%	148%	104%	0%	174%
1B	ABIETIC	50.8	38%	38%	169%	203%	24%	30%			29%	26%	28%	24%	61%	24%	203%
1B	NEOABIETIC	51.3	22%	0%	14%	23%	53%	0%			32%	42%	37%	0%	22%	0%	53%
1B	CHLORODEHYDROABIETIC	51.5	61%	51%	52%	54%	27%	48%			0%	0%	0%	0%	29%	0%	61%
1B	9,10-DICHLOROSTEARIC	50.5	45%	45%	12%	32%	18%	29%					0%	0%	23%	0%	45%
1B	DICHLORODEHYDROABIETIC	50.8	56%	59%	12%	14%	12%	13%			32%	25%	0%	0%	22%	0%	59%
1B	MEAN RECOVERY WITHIN SCAN		74%	67%	42%	51%	44%	59%			46%	43%	49%	51%			
1C	OLEIC	502.0	41%	39%	3%	5%	1%	5%			4%	5%	12%	17%	13%	1%	41%
1C	SANDARACOPIMARIC	503.5	66%	66%	11%	12%	7%	14%			10%	10%	15%	18%	23%	7%	66%
1C	ISOPIMARIC	502.0	74%	74%	8%	10%	8%	17%			9%	10%	17%	21%	25%	8%	74%
1C	PALUSTRIC/LEVOPIMARIC	1004.5	4%	4%	0%	0%	1%	2%			0%	0%	6%	5%	2%	0%	6%
1C	DYHYDROABIETIC	502.0	167%	168%	0%	0%	46%	63%			49%	51%	40%	46%	63%	0%	168%
1C	ABIETIC	503.0	7%	7%	62%	66%	2%	4%			0%	2%	8%	7%	17%	0%	66%
1C	NEOABIETIC	502.0	0%	0%	3%	5%	1%	0%			0%	0%	0%	0%	1%	0%	5%
1C	CHLORODEHYDROABIETIC	502.5	44%	44%	14%	16%	2%	8%			6%	0%	5%	7%	15%	2%	44%
1C	9,10-DICHLOROSTEARIC	504.0	41%	43%	3%	3%	3%	4%					0%	5%	13%	0%	43%
1C	DICHLORODEHYDROABIETIC	502.5	54%	56%	2%	2%	0%	3%			3%	4%	0%	0%	12%	0%	56%
1C	MEAN RECOVERY WITHIN SCAN		50%	50%	11%	12%	7%	12%			9%	10%	10%	13%			

REAGENT WATER: 1B - LOW SPIKE; 1C - HIGH SPIKE

DUPLICATE RESULTS: RES1 - REPLICATE #1, RES2 - REPLICATE #2

TABLE 2 - INTERLABORATORY STUDY 88-3: RESIN AND FATTY ACIDS
RESULTS EXPRESSED AS PERCENT RECOVERY OF DESIGN VALUE

DISTRIBUTED: NOVEMBER 28, 1988

SAMPLE#	PARAMETER	DESIGN (ppb)	LABORATORY NUMBER 6001 RES1	6001 RES2	6004 RES1	6004 RES2	6005 RES1	6007 RES1	6008A RES1	6008A RES2	6008B RES1	6008B RES2	6009 RES1	6009 RES2	MEAN	RANGE MIN	RANGE MAX
3B	LINOLENIC	51.0	0%	0%	455%	463%	0%	0%	0%	0%	0%	0%	0%	0%	76%	0%	463%
3B	OLEIC	52.0	22%	21%	21%	19%	6%	0%	0%	0%	0%	0%	19%	0%	9%	0%	22%
3B	SANDARACOPIMARIC	54.0	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
3B	ISOPIMARIC	52.0	26%	0%	0%	58%	0%	16%	0%	0%	0%	0%	0%	0%	8%	0%	58%
3B	PALUSTRIC/LEVOPIMARIC	103.1	0%	0%	0%	0%	0%	6%	0%	0%	0%	0%	0%	0%	1%	0%	6%
3B	DYHYDROABIETIC	53.5	0%	0%	32%	0%	0%	14%	0%	0%	0%	0%	0%	0%	4%	0%	32%
3B	ABIETIC	50.0	12%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	1%	0%	12%
3B	NEOABIETIC	51.3	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
3B	CHLORODEHYDROABIETIC	51.5	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
3B	9,10-DICHLOROSTEARIC	50.5	0%	0%	0%	0%	0%	0%					0%	0%	0%	0%	0%
3B	DICHLORODEHYDROABIETIC	50.8	24%	22%	0%	0%	0%	19%	0%	0%	0%	0%	0%	0%	5%	0%	24%
3B	MEAN RECOVERY WITHIN SCAN		8%	4%	46%	49%	1%	5%	0%	0%	0%	0%	2%	0%			
3C	OLEIC	439.3	12%	13%	16%	37%	7%	15%	9%	7%	13%	15%	10%	15%	15%	7%	37%
3C	SANDARACOPIMARIC	440.6	14%	15%	24%	55%	12%	21%	13%	7%	17%	18%	17%	13%	19%	6%	55%
3C	ISOPIMARIC	439.3	21%	21%	35%	81%	21%	33%	16%	10%	22%	23%	24%	18%	27%	10%	81%
3C	PALUSTRIC/LEVOPIMARIC	878.9	7%	7%	7%	19%	7%	6%	3%	0%	5%	6%	6%	4%	6%	0%	19%
3C	DYHYDROABIETIC	439.3	31%	27%	27%	58%	23%	44%	22%	15%	29%	33%	31%	24%	30%	15%	58%
3C	ABIETIC	440.1	9%	8%	60%	136%	7%	11%	0%	0%	9%	9%	12%	8%	22%	8%	136%
3C	NEOABIETIC	439.3	4%	3%	29%	10%	5%	0%	0%	0%	0%	0%	6%	5%	5%	0%	29%
3C	CHLORODEHYDROABIETIC	439.7	11%	12%	26%	59%	10%	19%	0%	0%	16%	22%	17%	13%	17%	0%	59%
3C	9,10-DICHLOROSTEARIC	441.0	12%	13%	10%	24%	12%	27%					11%	8%	15%	8%	27%
3C	DICHLORODEHYDROABIETIC	439.7	20%	21%	46%	101%	25%	31%	23%	19%	35%	39%	23%	17%	33%	17%	101%
3C	MEAN RECOVERY WITHIN SCAN		14%	14%	29%	50%	13%	21%	10%	6%	16%	18%	16%	13%			

PULP AND PAPER MILL EFFLUENT @2: 3B - LOW SPIKE; 3C - HIGH SPIKE DUPLICATE RESULTS: RES1 - REPLICATE #1, RES2 - REPLICATE #2

TABLE 2 - INTERLABORATORY STUDY 88-3: RESIN AND FATTY ACIDS
RESULTS EXPRESSED AS PERCENT RECOVERY OF DESIGN VALUE

DISTRIBUTED: NOVEMBER 28, 1988

SAMPLE#	PARAMETER	DESIGN (ppb)	LABORATORY NUMBER 6001 RES1	6001 RES2	6004 RES1	6004 RES2	6005 RES1	6007 RES1	6008A RES1	6008A RES2	6008B RES1	6008B RES2	6009 RES1	6009 RES2	MEAN	RANGE MIN	RANGE MAX
2B	LINOLENIC	51.0	0%	0%	0%	0%	0%	0%			0%	0%	0%	0%	0%	0%	0%
2B	OLEIC	52.0	10%	0%	0%	0%	0%	0%			0%	0%	17%	17%	5%	0%	17%
2B	SANDARACOPIMARIC	54.0	0%	0%	0%	0%	0%	0%			0%	0%	46%	43%	9%	0%	46%
2B	ISOPIMARIC	52.0	0%	0%	0%	0%	0%	0%			0%	0%	62%	60%	12%	0%	62%
2B	PALUSTRIC/LEVOPIMARIC	103.1	0%	0%	0%	0%	0%	0%			0%	0%	0%	0%	0%	0%	0%
2B	DYHYDROABIETIC	53.5	0%	0%	0%	0%	0%	0%			0%	0%	43%	0%	4%	0%	43%
2B	ABIETIC	50.8	0%	0%	0%	0%	0%	0%			0%	0%	0%	0%	0%	0%	0%
2B	NEOABIETIC	51.3	0%	0%	0%	0%	0%	0%			0%	0%	0%	0%	0%	0%	0%
2B	CHLORODEHYDROABIETIC	51.5	0%	0%	0%	0%	12%	0%			0%	0%	0%	0%	1%	0%	12%
2B	9,10-DICHLOROSTEARIC	50.5	0%	0%	0%	0%	0%	0%					0%	0%	0%	0%	0%
2B	DICHLORODEHYDROABIETIC	50.0	29%	25%	0%	0%	33%	0%			0%	0%	0%	0%	9%	0%	33%
2B	MEAN RECOVERY WITHIN SCAN		4%	2%	0%	0%	4%	0%			0%	0%	15%	11%			
2C	OLEIC	502.0	4%	5%	8%	4%	2%	2%	5%		6%	5%	38%	20%	9%	2%	38%
2C	SANDARACOPIMARIC	503.5	5%	14%	9%	6%	4%	2%	8%		9%	8%	48%	25%	12%	2%	48%
2C	ISOPIMARIC	502.0	6%	18%	12%	8%	6%	3%	11%		12%	13%	63%	32%	17%	3%	63%
2C	PALUSTRIC/LEVOPIMARIC	1004.5	1%	4%	1%	1%	1%	0%	0%		0%	0%	9%	5%	2%	0%	9%
2C	DYHYDROABIETIC	502.0	10%	24%	12%	8%	7%	4%	15%		14%	15%	89%	47%	22%	4%	89%
2C	ABIETIC	503.0	2%	6%	23%	16%	2%	1%	0%		0%	0%	20%	11%	7%	0%	23%
2C	NEOABIETIC	502.0	0%	2%	8%	4%	0%	0%	0%		0%	0%	5%	4%	2%	0%	8%
2C	CHLORODEHYDROABIETIC	502.5	4%	9%	5%	7%	3%	1%	0%		0%	0%	31%	16%	7%	0%	31%
2C	9,10-DICHLOROSTEARIC	504.0	5%	10%	0%	0%	4%	4%					30%	17%	9%	0%	30%
2C	DICHLORODEHYDROABIETIC	502.5	19%	27%	13%	10%	14%	12%	11%		20%	29%	45%	25%	21%	10%	45%
2C	MEAN RECOVERY WITHIN SCAN		6%	12%	9%	6%	4%	3%	5%		7%	8%	30%	20%			

PULP AND PAPER MILL EFFLUENT #1: 2B - LOW SPIKE; 2C - HIGH SPIKE

[illegible] RESULTS: RES1 - REPLICATE #1, RES2 - REPLICATE #2

FIGURE 1: INTERLABORATORY STUDY 88-3

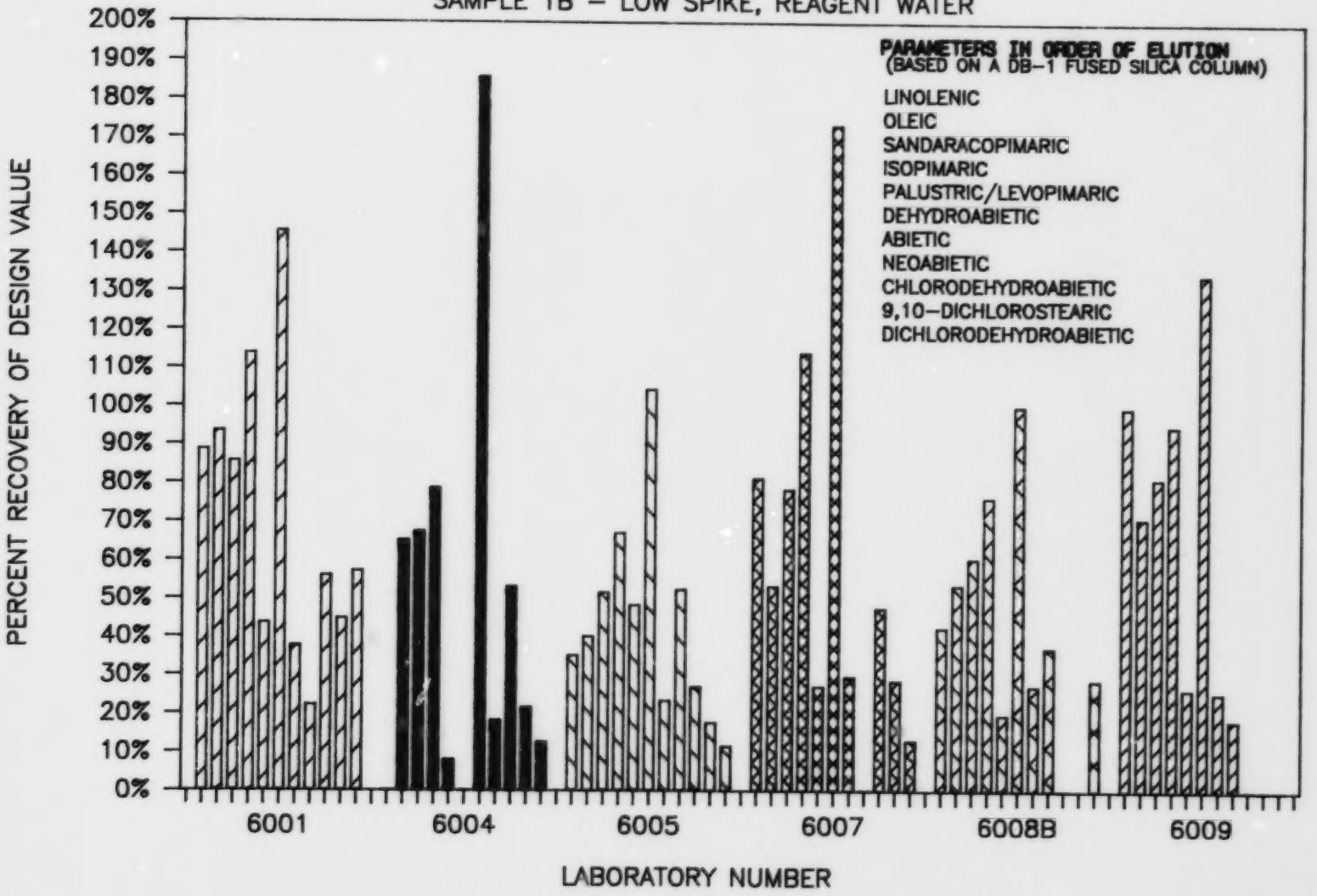


FIGURE 2: INTERLABORATORY STUDY 88-3

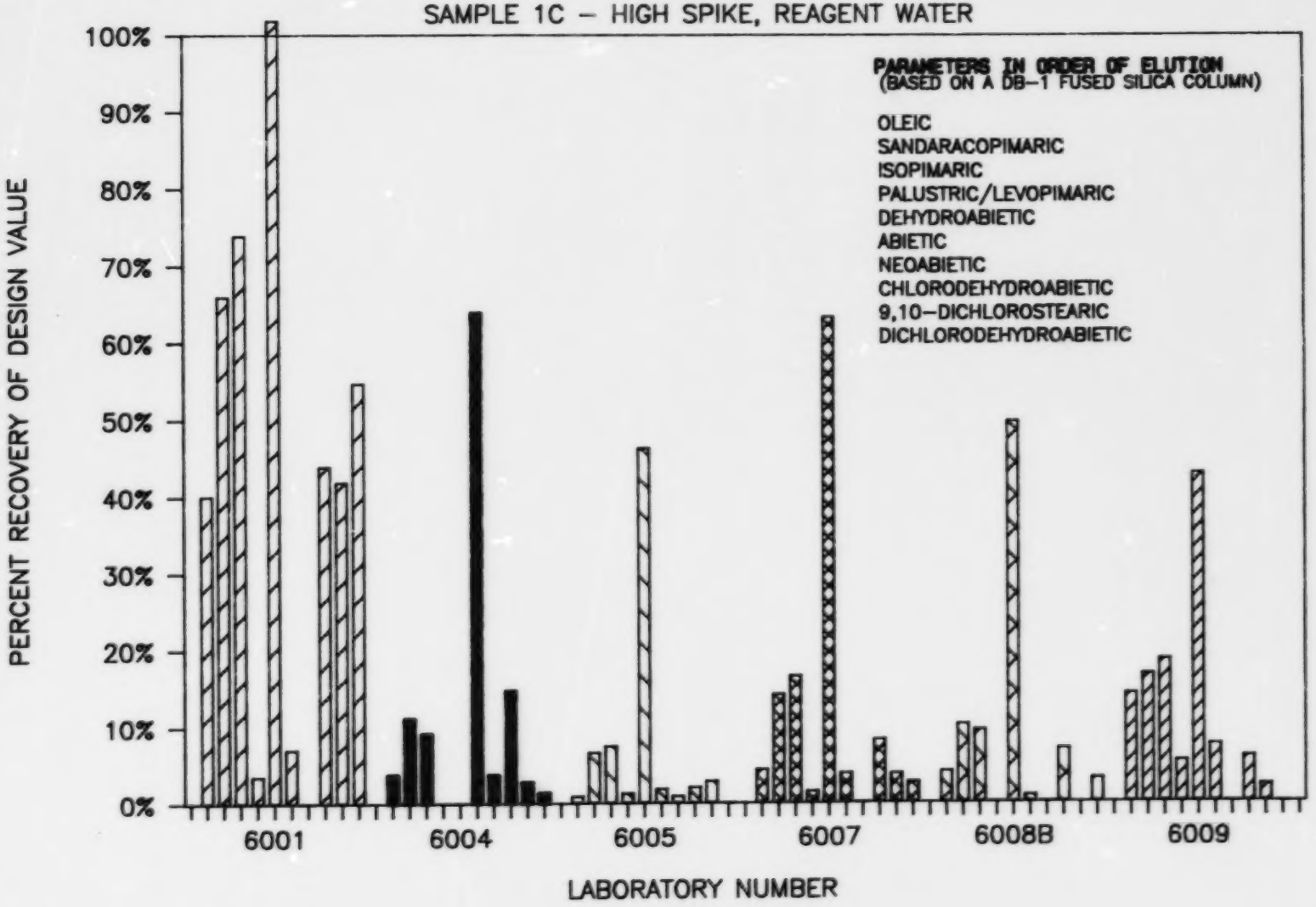


FIGURE 3: INTERLABORATORY STUDY 88-3

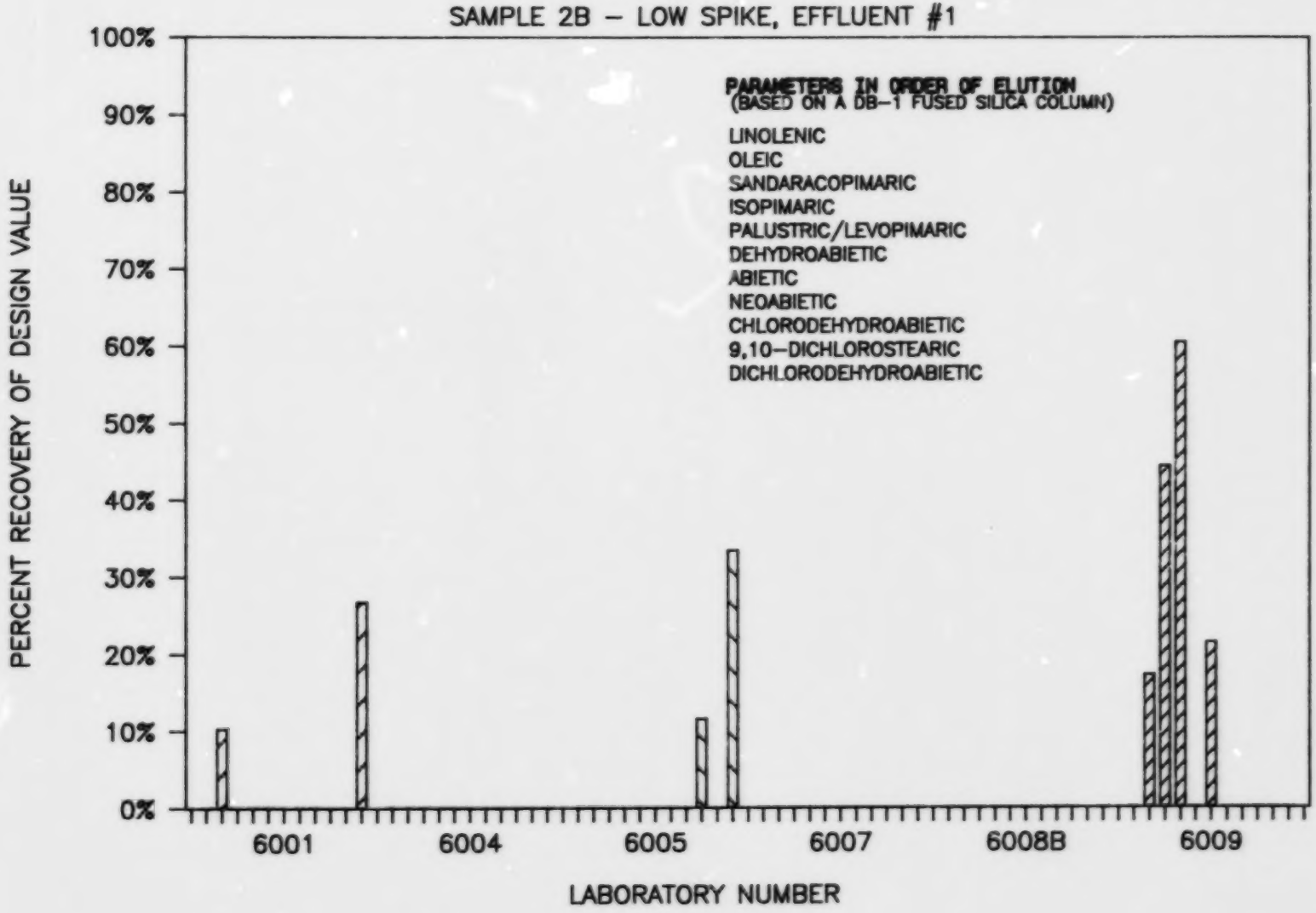


FIGURE 4: INTERLABORATORY STUDY 88-3

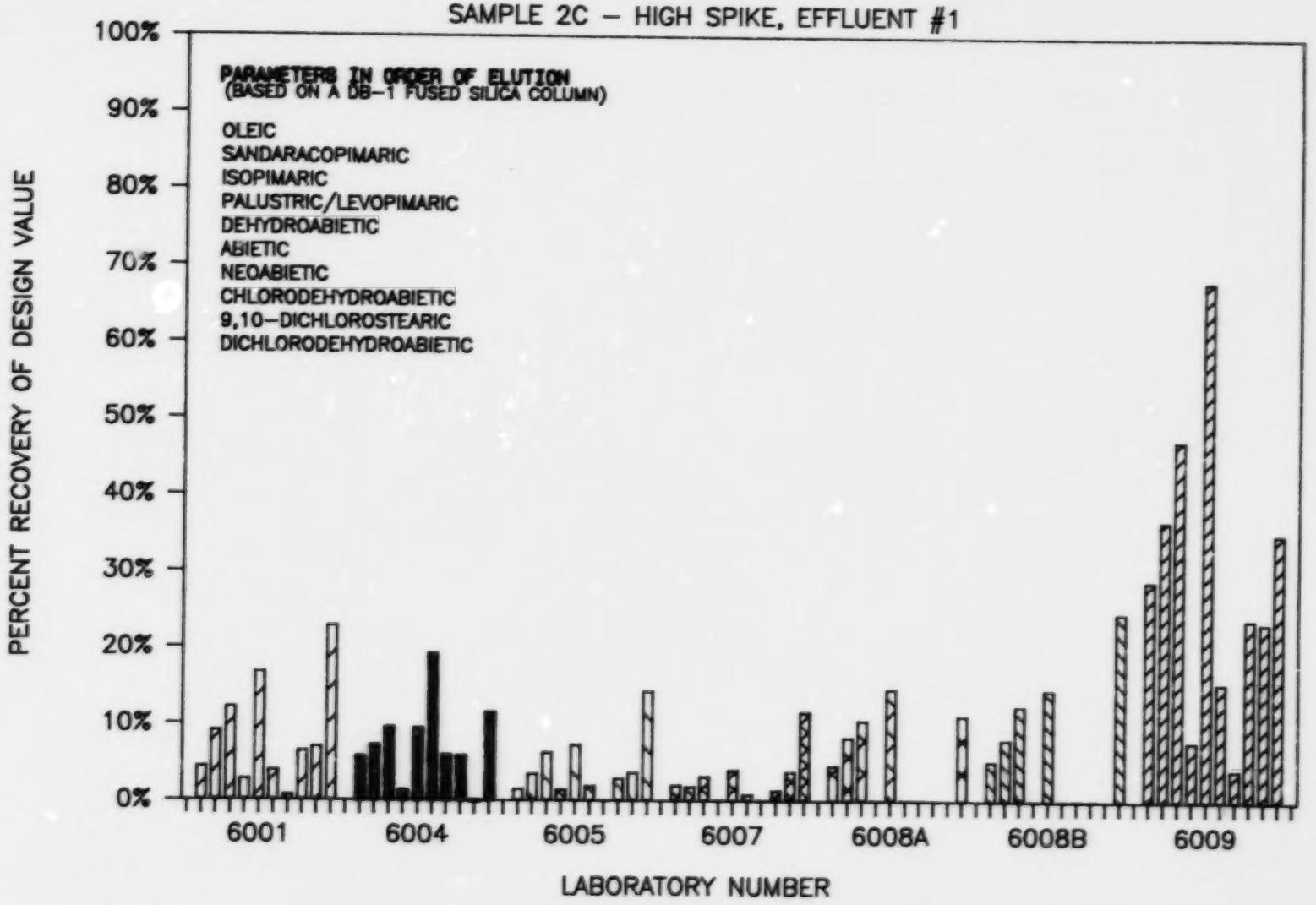


FIGURE 5: INTERLABORATORY STUDY 88-3

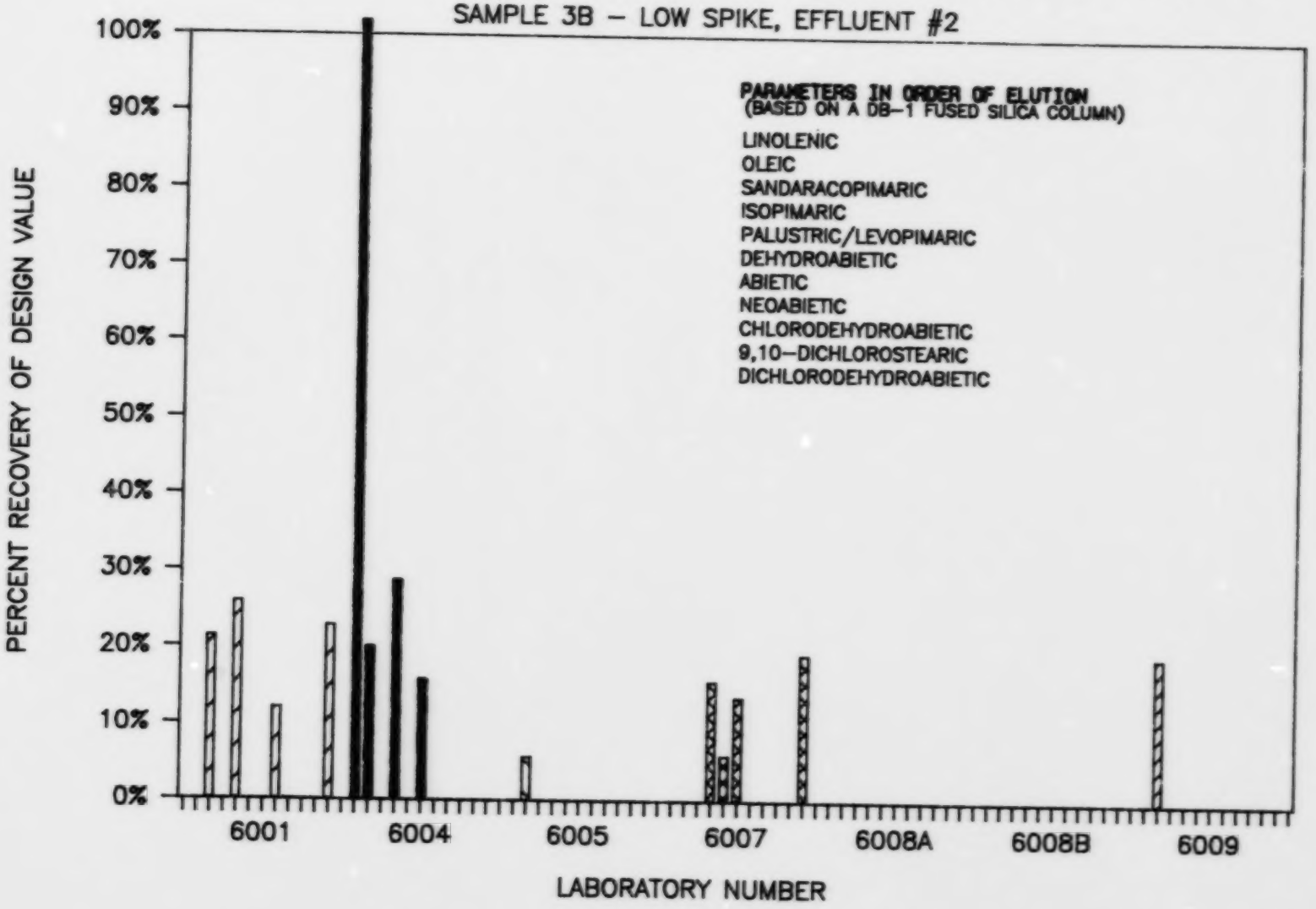


FIGURE 6: INTERLABORATORY STUDY 88-3

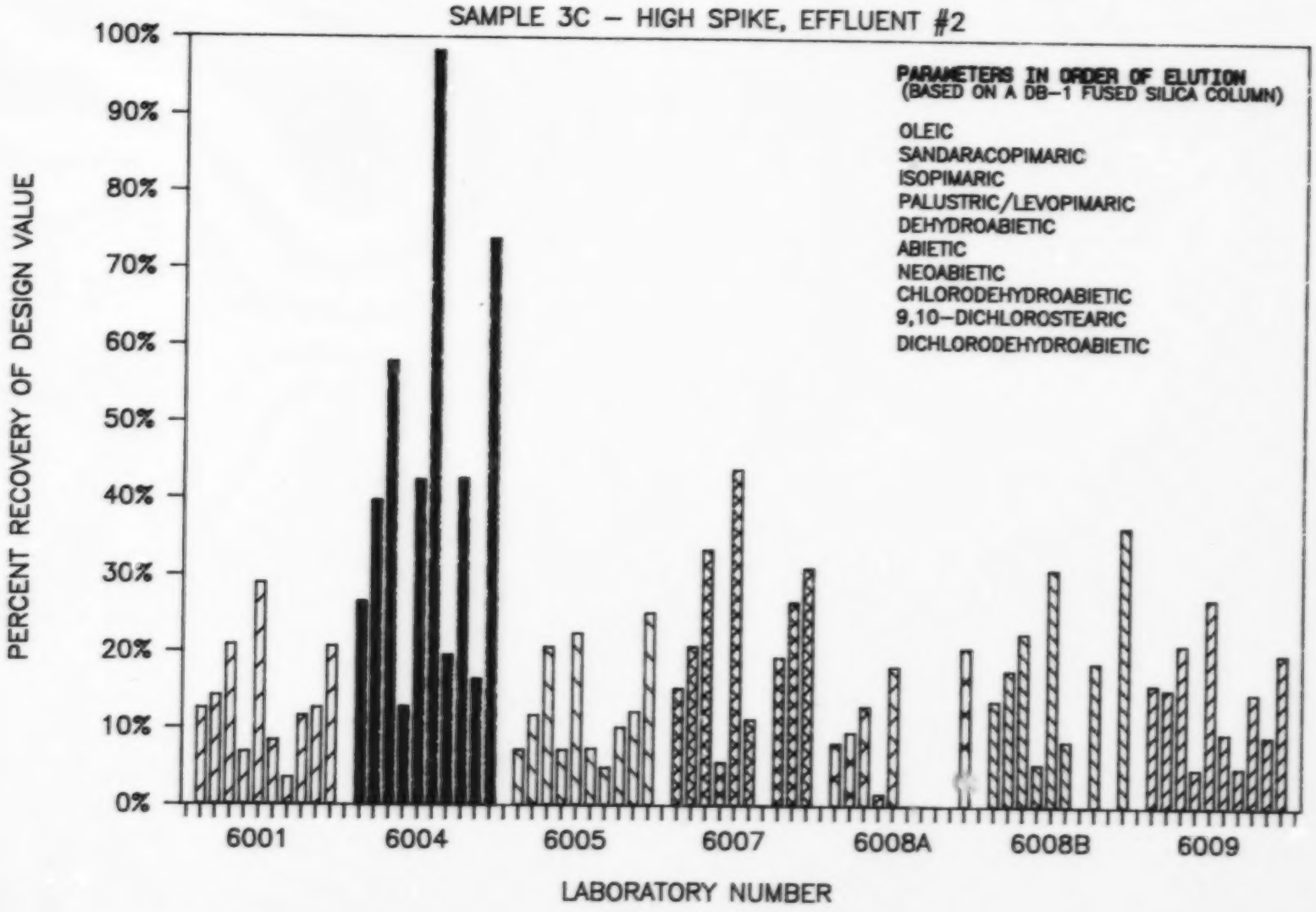
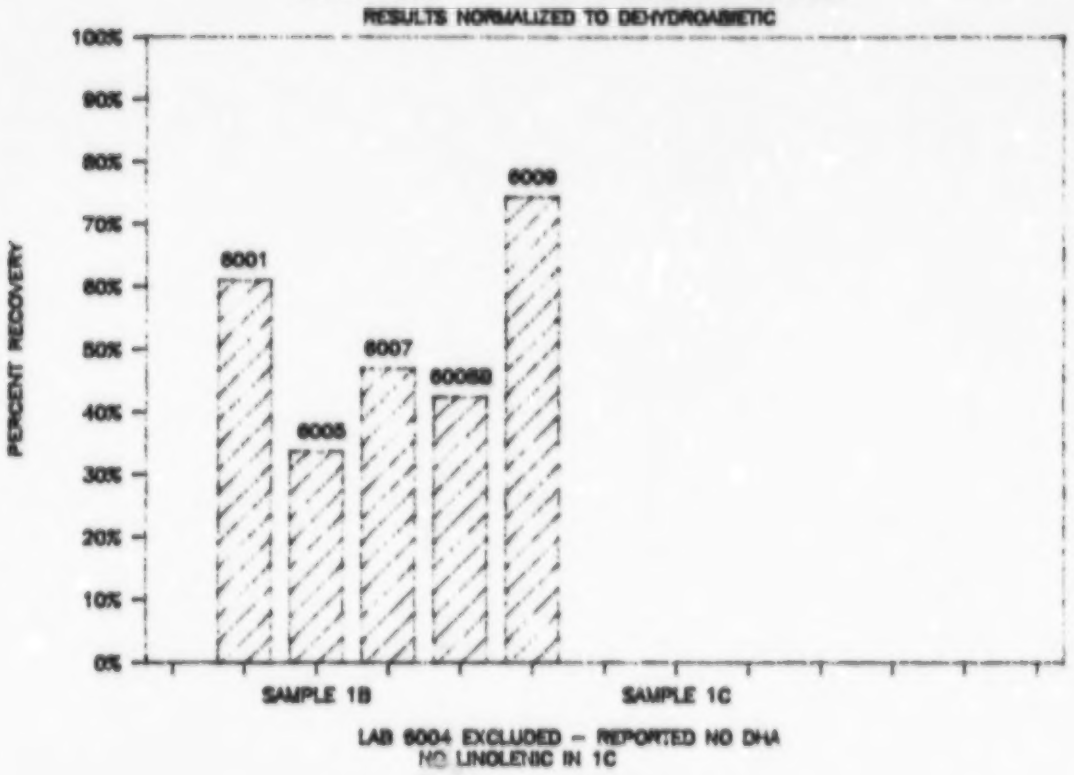
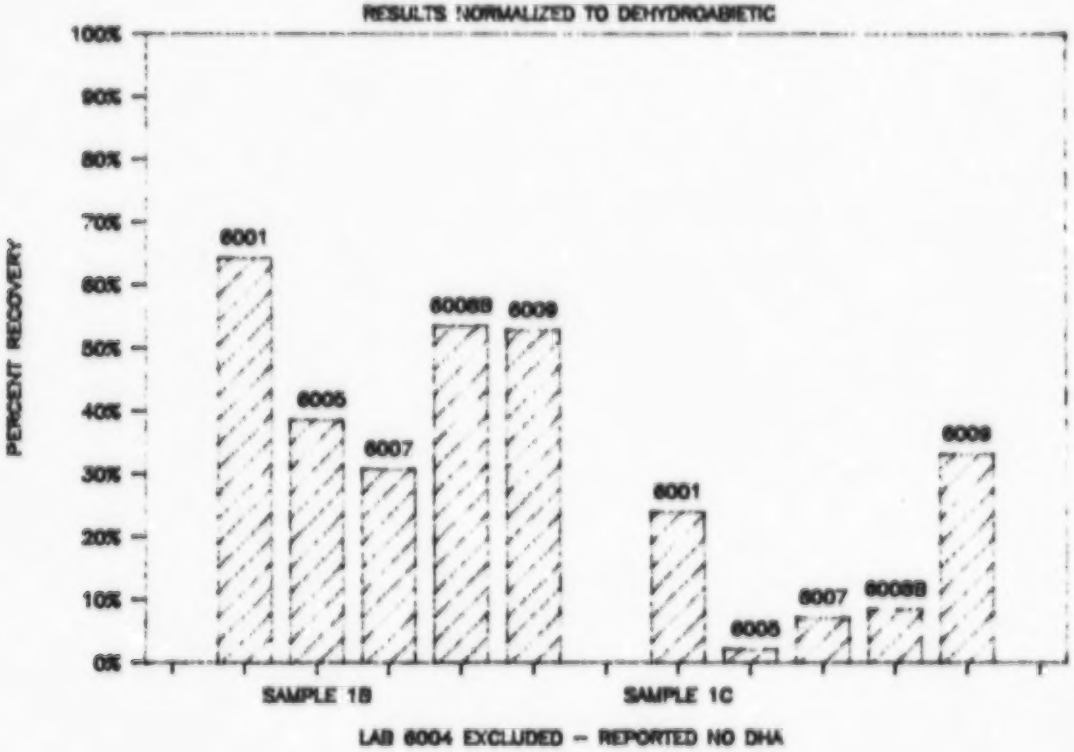


FIGURE 7: LINOLENIC ACID



LAB 6004 EXCLUDED – REPORTED NO DHA
NO LINOLENIC IN 1C

FIGURE 8: OLEIC ACID



LAB 6004 EXCLUDED – REPORTED NO DHA

FIGURE 9: SANDARACOPIMARIC ACID

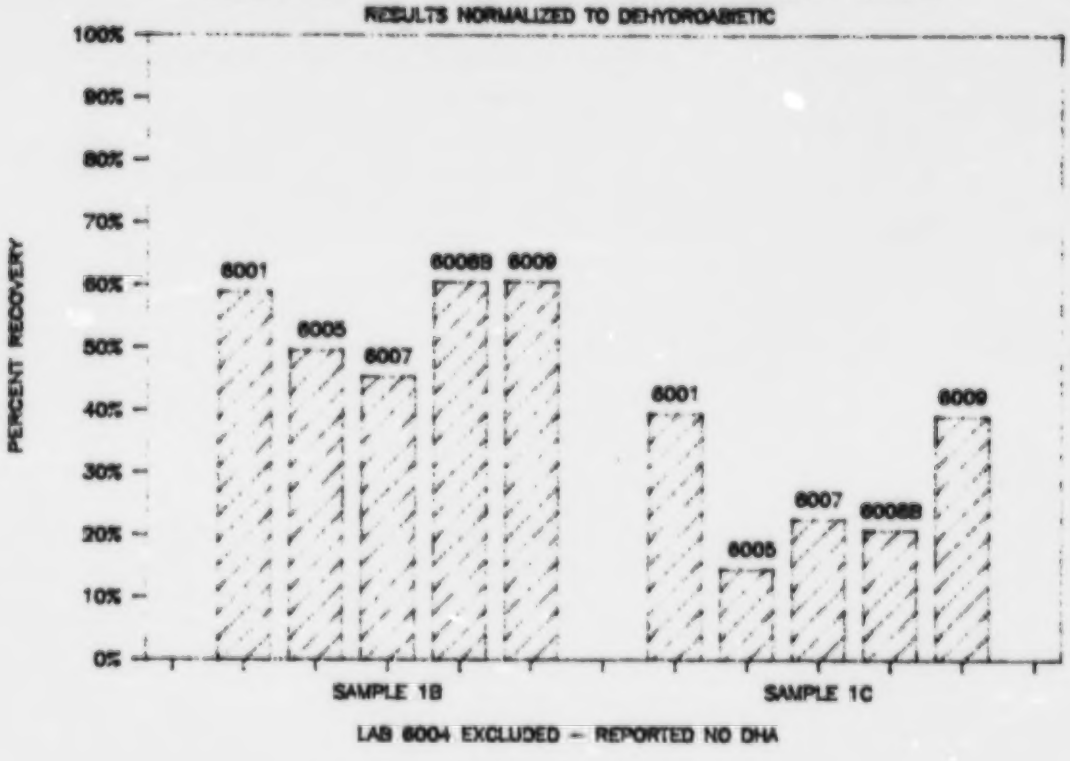


FIGURE 10: ISOPIMARIC ACID

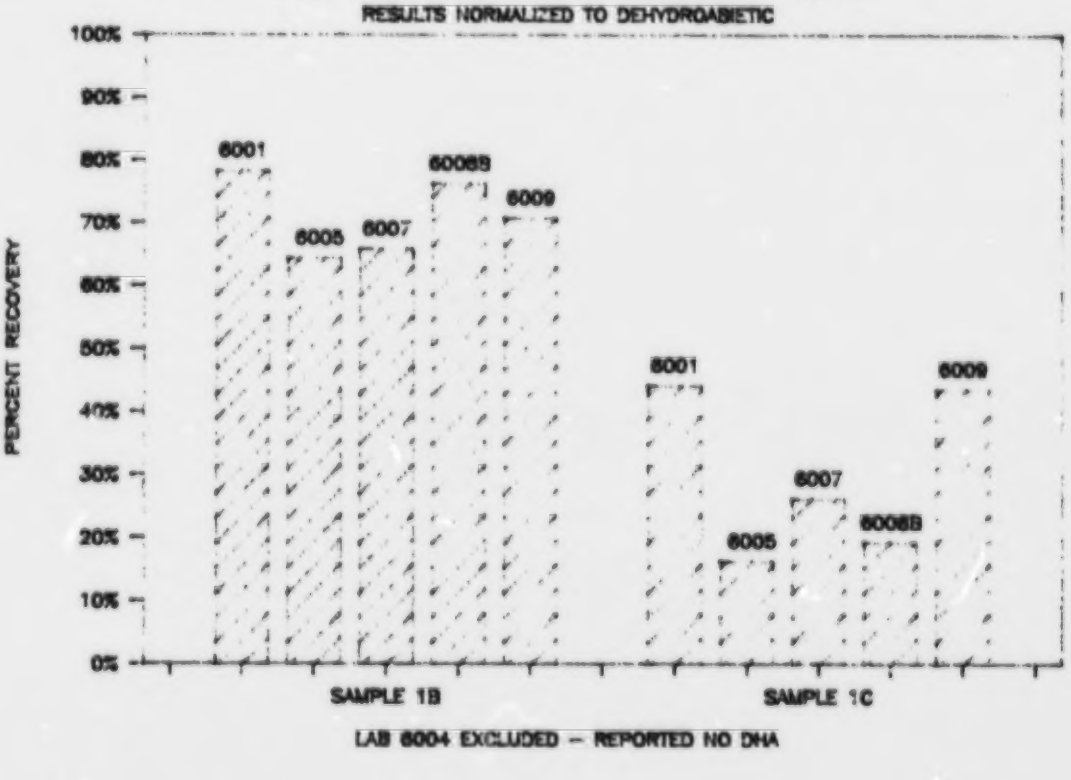


FIGURE 11: PALUSTRIC & LEVOPIMARIC

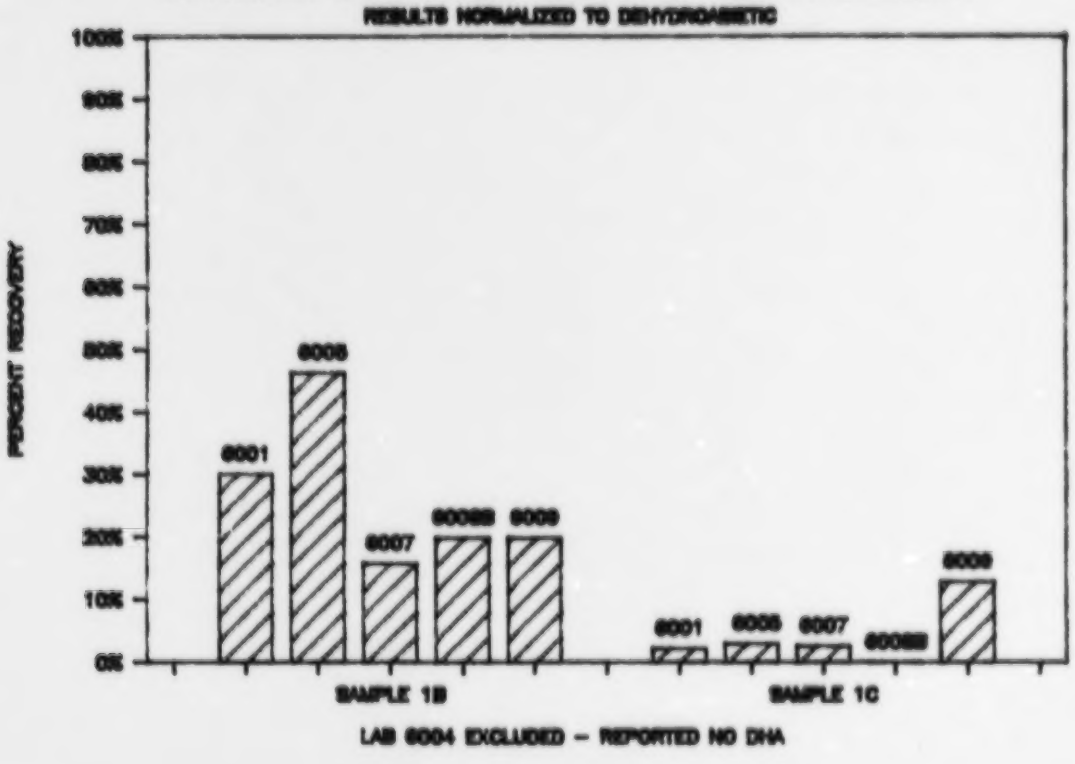


FIGURE 12: ABIETIC ACID

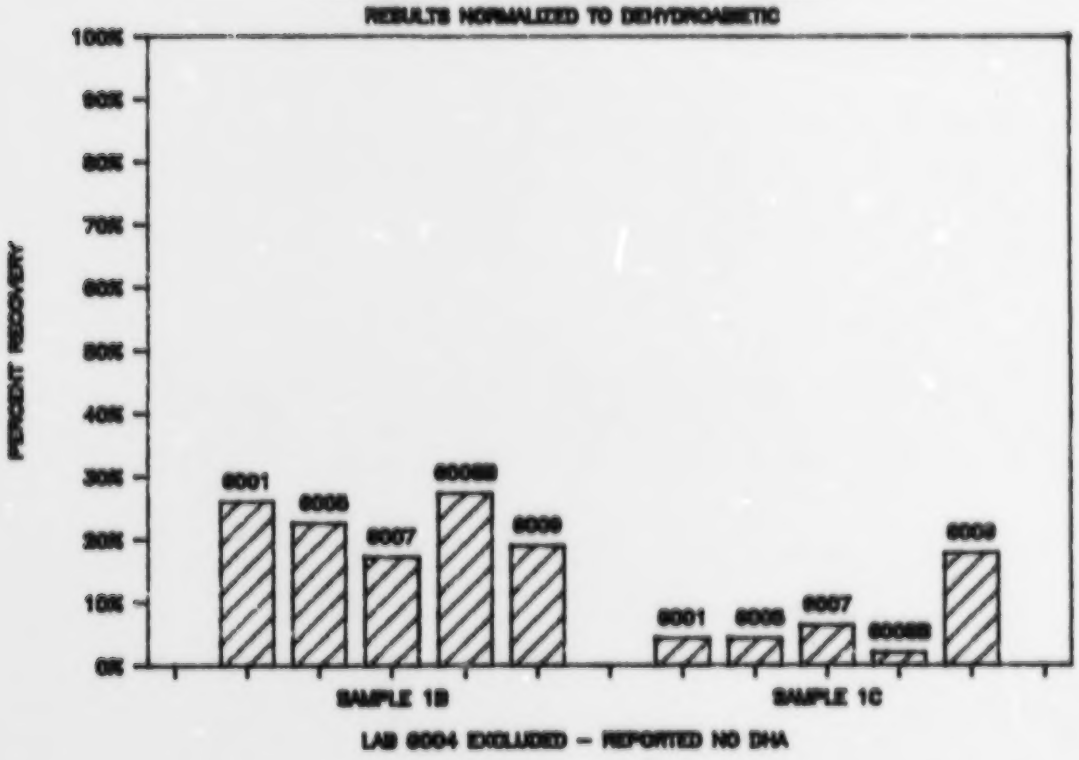


FIGURE 13: NEOABIETIC ACID

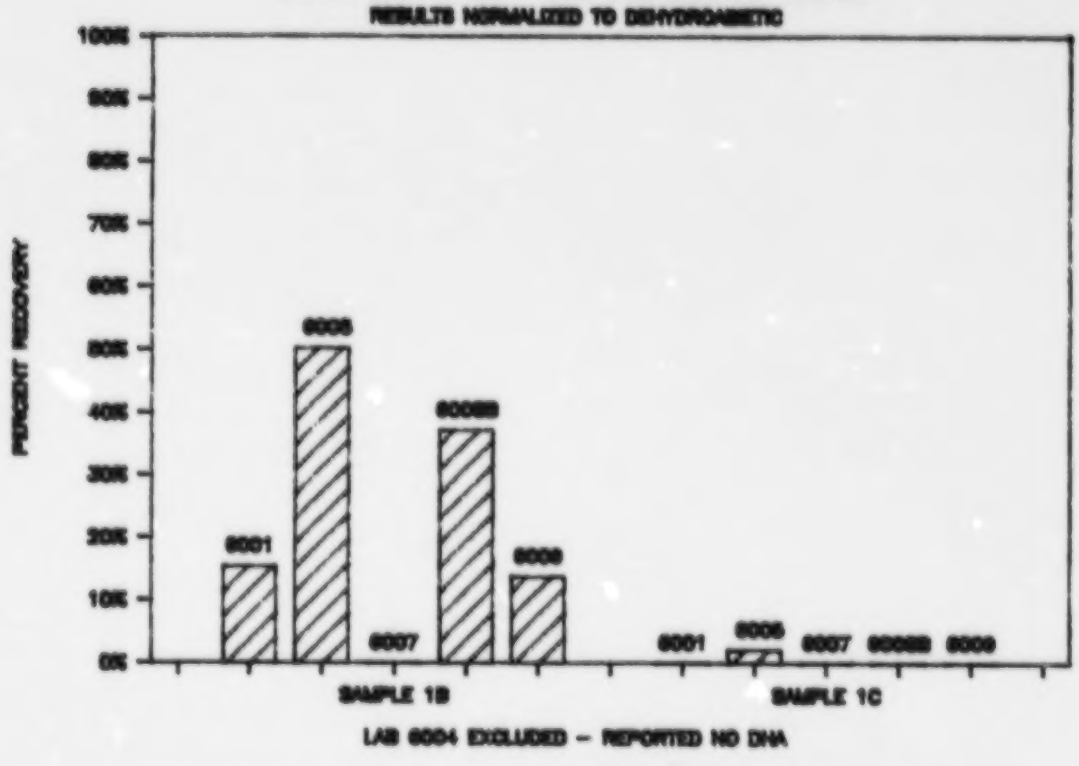


FIGURE 14: CHLORODEHYDROABIETIC ACID

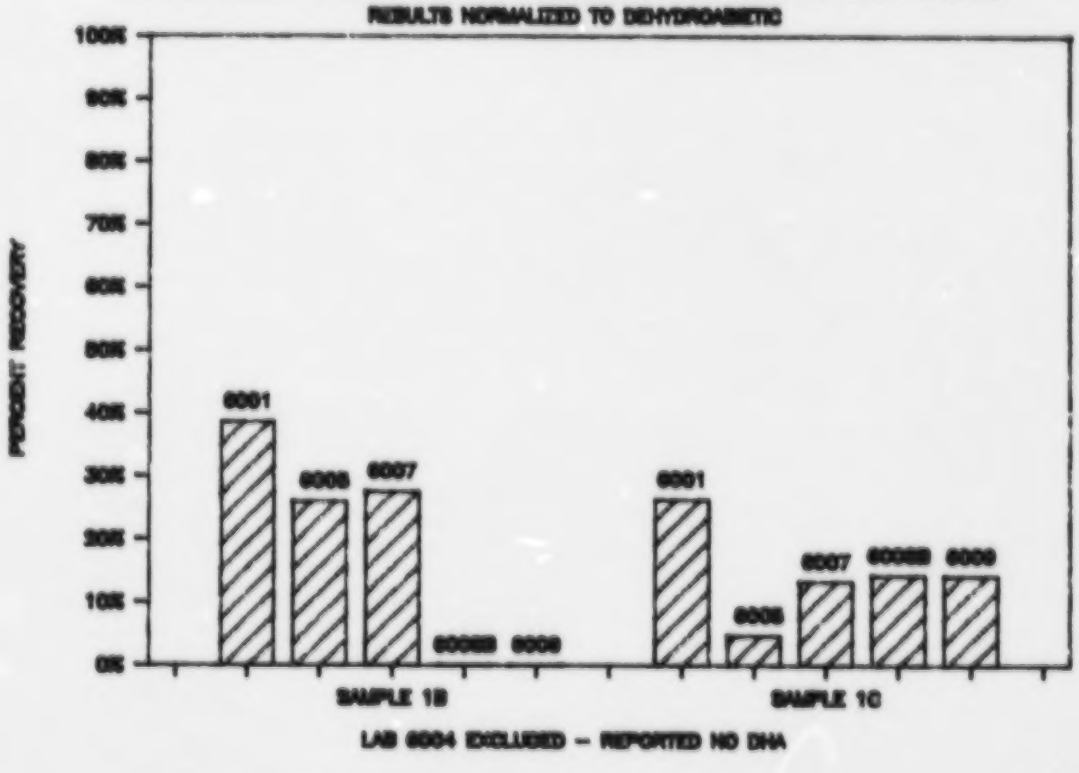


FIGURE 15: 9,10–DICHLOROSTEARIC ACID

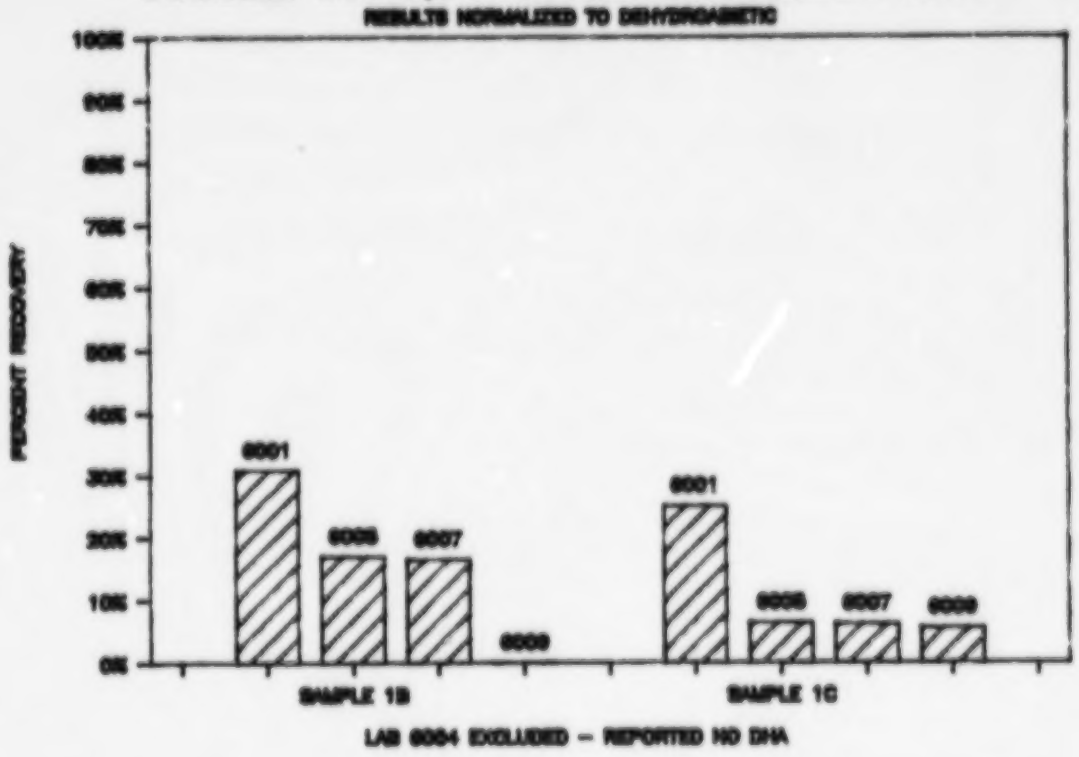


FIGURE 16: DICHLORODEHYDROABIETIC ACID

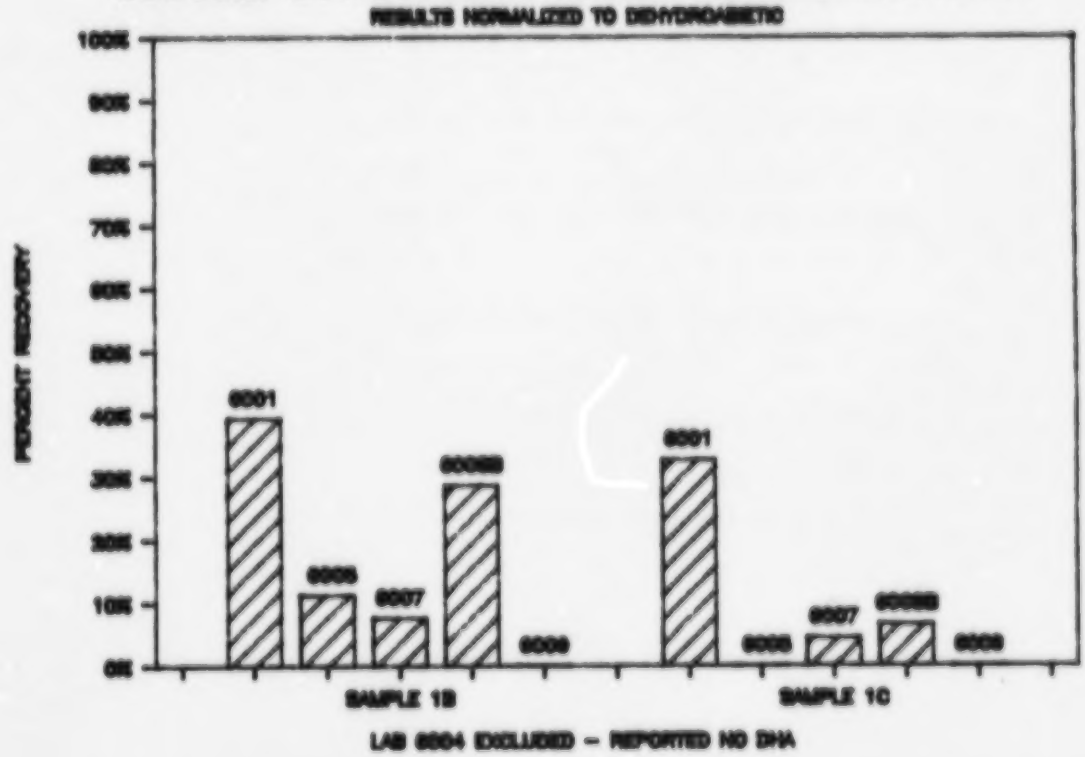
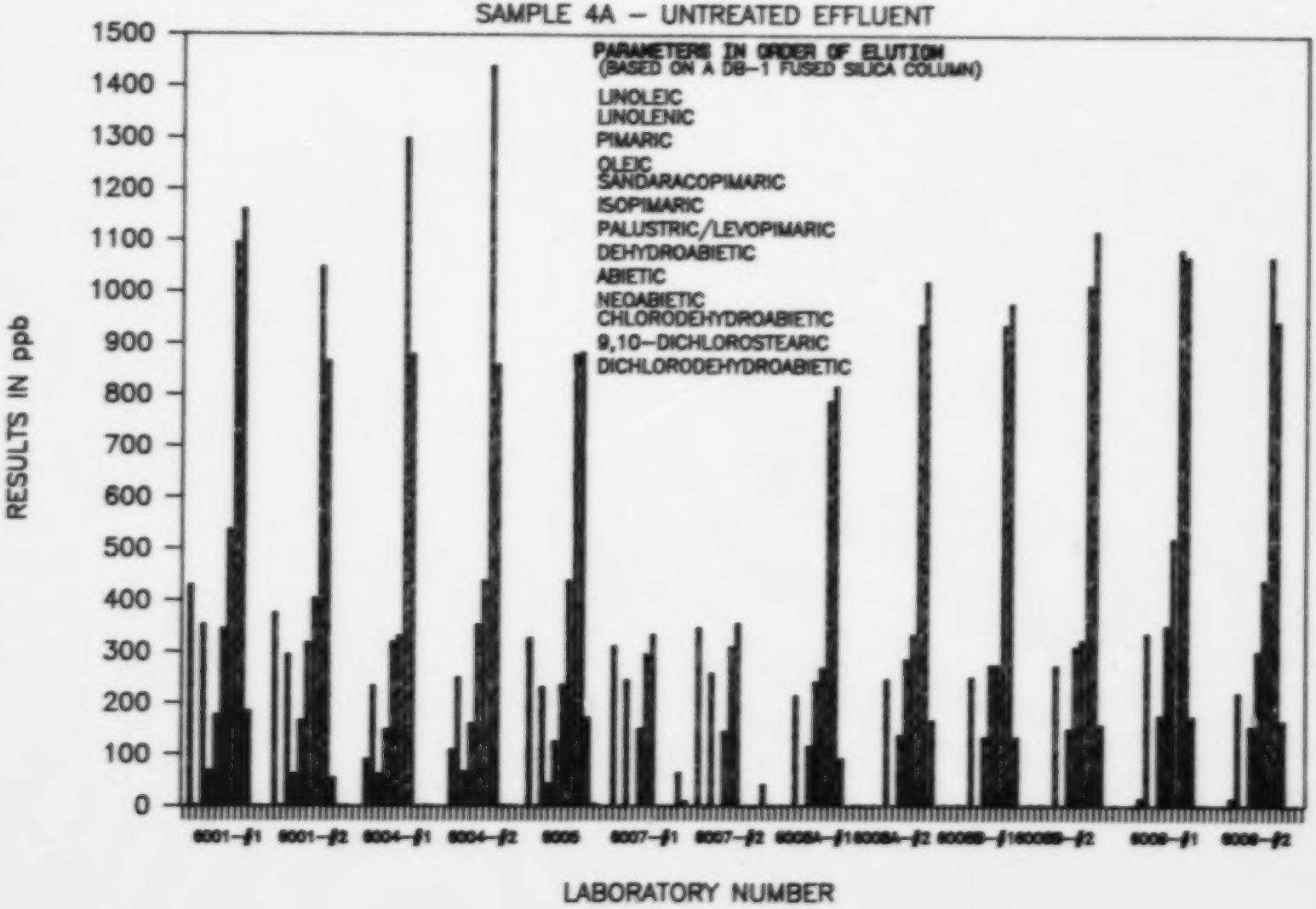


FIGURE 17: INTERLABORATORY STUDY 88-3



8 APPENDIX 2 - LIST OF PARTICIPANTS AND CORRESPONDENCE

List of Participants

Pulp and Paper Institute of Canada
570 St. John's Blvd.
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H9R 3J9
(514) 630-4100

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(604) 224-4331

Contact: Dr. Jim McKinley

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Contact: Mr. Peter Fowlie

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Contact: Mr. Aziz Shariff

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Bedford Institute of Oceanography
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(902) 426-6191

Contact: Mr. Peter Henniger

Ontario Ministry of the Environment
Laboratory Services Branch
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Rexdale, Ontario
M9W 5L1
(416) 235-5760

Contact: Mrs. Yvonne Jones

Beak Analytical Services
14 Abacus Road
Brampton, Ontario
L6T 5B7
(416) 458-4044

Contact: Mr. John Robertson

RESIN ACID ROUND ROBIN NOTIFICATION
PHASE 2: November 10, 1988

INTRODUCTION

This document is a formal notification of Phase 2 of the Resin and Fatty Acid Method Development Round Robin being conducted by the Ontario Ministry of the Environment on behalf of the MISA Pulp and Paper Analytical Working Group. All participants of Phase 1, conducted in June, 1988 are invited to participate in Phase 2. It is hoped that full participation from the invited laboratories may occur.

METHODOLOGY

The same method as was used for Phase 1 is to be used for Phase 2. Any participating laboratories who require an additional copy of the draft method should contact Sylvia Cussion at (416) 235-5842 or Steve Burns at (416) 235-5932.

Please note that the MISA working group requests that the method be followed as closely as possible. This is particularly important in the use of the detector on the gas chromatograph. The method specifies GC-FID and we request that only this detector be used.

SCHEDULE

During the week of November 28, 1988, participating laboratories will receive nine (9) spiked samples containing the following resin acids:

Sandaracopimaric Acid	Isopimaric Acid
Palustric Acid	Levopimaric Acid
Dehydroabietic Acid	Abietic Acid
Neoabietic Acid	Chlorodehydroabietic Acid
Dichlorodehydroabietic Acid	Oleic Acid
Linolenic Acid	9,10-Dichlorostearic Acid

All samples are to be extracted and analyzed according to the procedures in the draft method. The samples will consist of high and low spikes, plus blanks in distilled water and two different pulp and paper effluents.

An additional sample will be included in the round robin. It will be a typical pulp and paper effluent but it will not be spiked with additional resin and fatty acids.

Samples must be stored at 4 degrees Celcius upon receipt. Samples must be extracted within seven (7) days. The pH should not be adjusted until just prior to extraction (this differs slightly from section 9.2 of the draft method). Analysis of the extract should take place as soon after extraction as possible. Results should be reported no later than January 6, 1989 to Sylvia Cussion at the following address:

Ministry of the Environment
Laboratory Services Branch
Computer Systems - QA/QC Section
125 Resources Rd.
Rexdale, Ontario, M9W 5L1

SUMMARY OF RESULTS

All participating laboratories will be assigned an identification code. All laboratories will receive a complete set of the results from Phase 2. All laboratories will be identified only by their identification code. Conclusions drawn by the Analytical Working Group and recommendations made will also be provided to the participating laboratories.

No further notice is to be given prior to distribution of the samples. Should a laboratory wish to withdraw from this round robin, or if there are any difficulties with the above schedule, please contact Sylvia Cussion immediately at (416) 235-5842.

Ontario Ministry of the Environment
Laboratory Services Branch
LCS-QA/QC Section
125 Resources Rd.
Rexdale, Ontario
M9W 5L1

(416) 235-5842
FAX (416) 235-5744

November 28, 1988.

TO: PARTICIPANTS OF RFA ROUND ROBIN (Phase 2)

Please find enclosed ten (10) 1 litre amber bottles labelled 1A, 1B, 1C, 2A, 2B, 2C, 3A, 3B, 3C, and 4A. If you are missing any of the above items, please contact me at the above phone number immediately. Store all samples at 4 degrees Celcius until ready for extraction. Do not adjust the pH until just prior to extraction.

Samples 1B, 2B, and 3B have been spiked with the following compounds:

- Sandaracopimaric Acid
- Palustric Acid
- Abietic Acid
- Chlorodehydroabietic Acid
- Dichlorodehydroabietic Acid
- Linolenic Acid
- Isopimaric Acid
- Levopimaric Acid
- Neoabietic Acid
- Oleic Acid
- 9,10-Dichlorostearic Acid

Samples 1C, 2C, and 3C have been spiked with the following compounds:

- Sandaracopimaric Acid
- Palustric Acid
- Abietic Acid
- Chlorodehydroabietic Acid
- Dichlorodehydroabietic Acid
- Isopimaric Acid
- Levopimaric Acid
- Neoabietic Acid
- Oleic Acid
- 9,10-Dichlorostearic Acid

These samples are to be extracted within seven (7) days of reception and analyzed as soon as possible thereafter. The results should be forwarded to me no later than January 6, 1989.

Please report all results as µg/L (ppb). To aid the MISA working group's interpretation of the results, please include a copy of the sample chromatograms, your response factor and calculations for Dehydroabietic Acid, and any variations used from the Draft Method. Please let me know if there were any problems analyzing any of the samples.

Your lab identification code is:

Please contact me if there are any questions.

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist

Ontario Ministry of the Environment
Laboratory Services Branch
LCS-QA/QC Section
125 Resources Rd.
Rexdale, Ontario
M9W 5L1

(416) 235-5842

June 6, 1989.

TO: PARTICIPANTS OF MOE INTER-LABLABORATORY STUDY 88-3

Thank you for your participation in the MOE Inter-Laboratory Study 88-3 conducted in November 1988 on behalf of the Pulp and Paper Sector MISA Analytical Working Group. Originally named RFA Round Robin (Phase 2), it has been renamed to reflect our new numbering scheme. Your participation is greatly appreciated by the MISA Analytical Working Group.

Attached are all the results reported to me as of the end of February, 1989. Not all the original participants were able to report results. Listed for each sample and parameter are the expected values, the results reported by each participant, the mean, minimum result, maximum result, and the standard deviation. For labs that did not report a result for a specific parameter for all samples, the space has been left blank. For labs that reported results for a parameter, but did not report a result in a particular sample, the result was reported as "0". All participants are identified only by their identification code.

A formal report is presently being written, but I regret that it will not be completed until August 1989. All participants will receive a copy as soon as it becomes available.

Please contact me if you have any further questions.

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist

Attachment